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An Investigation of Main Group Metal Derivatives of
Cobalt Carbonyl and Related Compounds

by

David John Patmore



A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE
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DEPARTMENT OF CHEMISTRY

EDMONTON, ALBERTA

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THE UNIVERSITY OF ALBERTA
FACULTY OF GRADUATE STUDIES

The undersigned certify that they have read, and
recommended to the Faculty of Graduate Studies for acceptance,
a thesis entitled

AN INVESTIGATION OF MAIN GROUP METAL DERIVATIVES OF

COBALT CARBONYL AND RELATED COMPOUNDS

submitted by David John Patmore, B.Sc., in partial fulfilment
of the requirements for the degree of Doctor of Philosophy.

ABSTRACT

Numerous tetracarbonylcobalt derivatives of germanium and tin have been synthesized by displacement of halide ions from organometallic halides with the tetracarbonylcobaltate(-I) anion, and by the reaction of cobalt carbonyl with metal tetrahalides and organometallic halides. In this way it was possible to prepare the complete series of compounds

$R_m X_{4-m-n} Sn[Co(CO)_4]_n$ (where $n = 1, 2, 3$, and 4 , $m < 4-n$, $R = Ph, Me$ and $X = Cl, Br, I$), in which tin is bonded directly to cobalt, as well as the compounds $R_n X_{3-n} GeCo(CO)_4$ and $R_n X_{2-n} Ge[Co(CO)_4]_2$ involving Ge-Co bonds.

Similar anion displacement reactions have been used to prepare tetracarbonylcobalt derivatives of gallium, indium, and thallium, such as $Br_2 GaCo(CO)_4 \cdot THF$, $BrIn[Co(CO)_4]_2$ and $Tl[Co(CO)_4]_3$, (THF = tetrahydrofuran).

A general investigation of insertion reactions was carried out. These involved reaction between a transition metal carbonyl complex possessing a metal-metal or metal-halogen bond and such compounds as $SnCl_2$, GeI_2 and $InBr$. The products of these reactions were compounds in which the main group metal had inserted in the metal-metal or metal-halogen bond. Thus $Co_2(CO)_8$ reacted with $SnCl_2$ and $InBr$ to give $Cl_2 Sn[Co(CO)_4]_2$ and $BrIn[Co(CO)_4]_2 \cdot THF$

respectively, while $\text{IMo(CO)}_3\text{Cp}$ and InI gave $\text{I}_2\text{InMo(CO)}_3\text{Cp} \cdot \text{THF}$. For such reactions to occur the main group metal must be capable of increasing its oxidation number by two units, and be able to form a stable bond to the transition metal.

The infrared spectra in the carbonyl stretching region of many tetracarbonyl derivatives were investigated. The compounds $\text{R}_n\text{X}_{3-n}\text{MCo(CO)}_4$ were found to possess three or four bands in the carbonyl stretching region depending on whether the symmetry was C_{3v} or C_s respectively, in accord with group theory arguments. The electronegativity of groups attached to M was found to have a marked influence upon the carbonyl frequencies, an increase of electronegativity causing an increase in carbonyl stretching frequency. This was explained in terms of variations in electron withdrawing ability of $\text{R}_n\text{X}_{3-n}\text{M}$ operating via metal-cobalt σ - and π -bonding.

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CHAPTER I

A Review of Compounds Involving Bonds Between Main and Transition Metals

The following brief review of the study of compounds in which a main group metal is directly bonded to a transition metal illustrates the rapid increase in interest in this field during the past 40 years, and indicates the present state of our knowledge of these compounds. It is not, however, intended to be an exhaustive study of all previous work in this field.

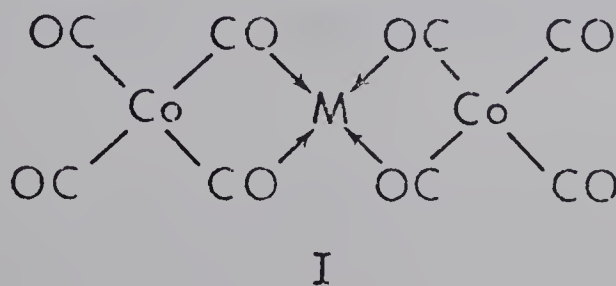
In this work the term "main group metal" is applied to all non-transition metals, in particular when referring to the following groups of metals: Cu, Ag, Au, Zn, Cd, Hg; Ga, In, Tl; and Ge, Sn, Pb. In order to avoid confusion by use of the A and B subgroup notation, these groups of metals will be referred to as Groups I to IV.

1. Historical Survey

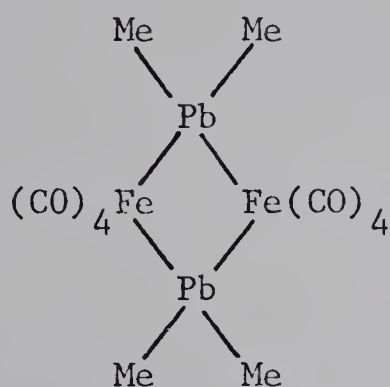
Compounds which possess bonds between main and transition metals have been known for at least 40 years but not until very recently were the structures of such compounds known with certainty. The first examples appear to have been reported by Hock and Stuhlman (1,2,3) in 1928 who prepared various mercury derivatives of iron carbonyl such as $\text{Fe}(\text{CO})_4\text{Hg}_2\text{Cl}_2$ and $\text{HgFe}(\text{CO})_4$ by the reaction of iron pentacarbonyl with mercury salts. The structure of the bromo analogue of the first compound has now

been determined (4) and was shown to be cis-(BrHg)₂Fe(CO)₄ with two Hg-Fe bonds. Later, in 1933, Feigl and Krumholz (5) reported some cadmium derivatives of iron carbonyl which were formulated as CdFe(CO)₄, (NH₃)₂CdFe(CO)₄ and Py₂CdFe(CO)₄, and which were prepared by reaction of cadmium acetate and base on Fe(CO)₅. In the same year, AgCo(CO)₄ was described by Schubert (6), and four years later Hieber and Schulten (7) reported dipyAgCo(CO)₄ and Hg[Co(CO)₄]₂, the latter compound possessing two colinear Hg-Co bonds as shown by a recent X-ray structure determination (8).

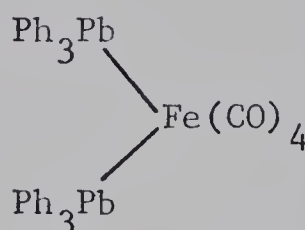
In 1942 Hieber and Teller (9) described the preparation of a series of main group metal derivatives of cobalt carbonyl. These were prepared by treating a mixture of cobalt metal or cobalt bromide and main group metal with high pressure carbon monoxide at elevated temperatures. Prepared in this way were: M[Co(CO)₄]₂ (M = Zn, Cd, Hg and Sn), TlCo(CO)₄, Tl[Co(CO)₄]₃ and In[Co(CO)₄]₃. It was suggested by these authors that the structures of these compounds involved carbonyl bridges between cobalt and the other metal, as shown in I. This view is no longer tenable.



The first suggestion of the possibility of metal-metal bonding in these compounds appears to have been made in 1947 by Hein and Heuser (10) who prepared a series of organo-lead derivatives of iron carbonyl such as $[\text{Me}_2\text{PbFe}(\text{CO})_4]_2$ and $(\text{Ph}_3\text{Pb})_2\text{Fe}(\text{CO})_4$ for which the very plausible structures II and III were postulated.



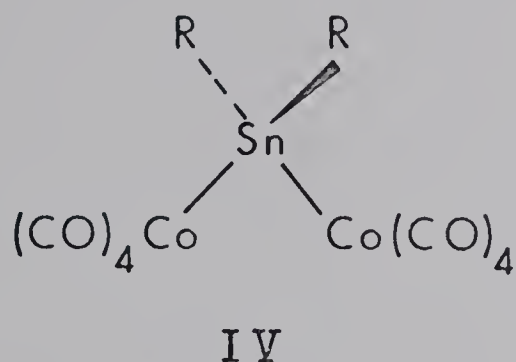
II



III

Later, in 1955, Fischer et al. (11) also suggested the existence of main to transition metal bonds in the mercury derivatives $\text{Hg}[\text{M}(\text{CO})_3\text{Cp}]_2$, when $\text{M} = \text{Cr}, \text{Mo}$ and W , in which they postulated the M-Hg-M bond sequence.

Some organotin derivatives of cobalt carbonyl were reported in 1956 by Hieber and Breu (12,13) who prepared $\text{Bu}_3\text{SnCo}(\text{CO})_4$, $\text{Bu}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$ and $\text{Me}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$ by treating organotin halides with $\text{NaCo}(\text{CO})_4$. Again they postulated bridges between tin and cobalt, but today cobalt-tin bonded structures such as IV would be written.



These last two reports (11,12) heralded the beginnings of a rapidly increasing interest in this field, to which added impetus was given by the work of Gorsich (14) who studied the preparation of various tin and lead derivatives of manganese pentacarbonyl such as $\text{Ph}_3\text{SnMn}(\text{CO})_5$ and $\text{Me}_2\text{Sn}[\text{Mn}(\text{CO})_5]_2$, by the reaction of $\text{NaMn}(\text{CO})_5$ on organotin halides. This rapid increase is illustrated graphically in Figure I which shows the number of different main to transition metal bonds known as a function of time. The growth is almost exponential, and is very rapid after 1962. The total to date probably exceeds 100 while the total number of compounds involved is much larger.

A summary of all the different main to transition metal

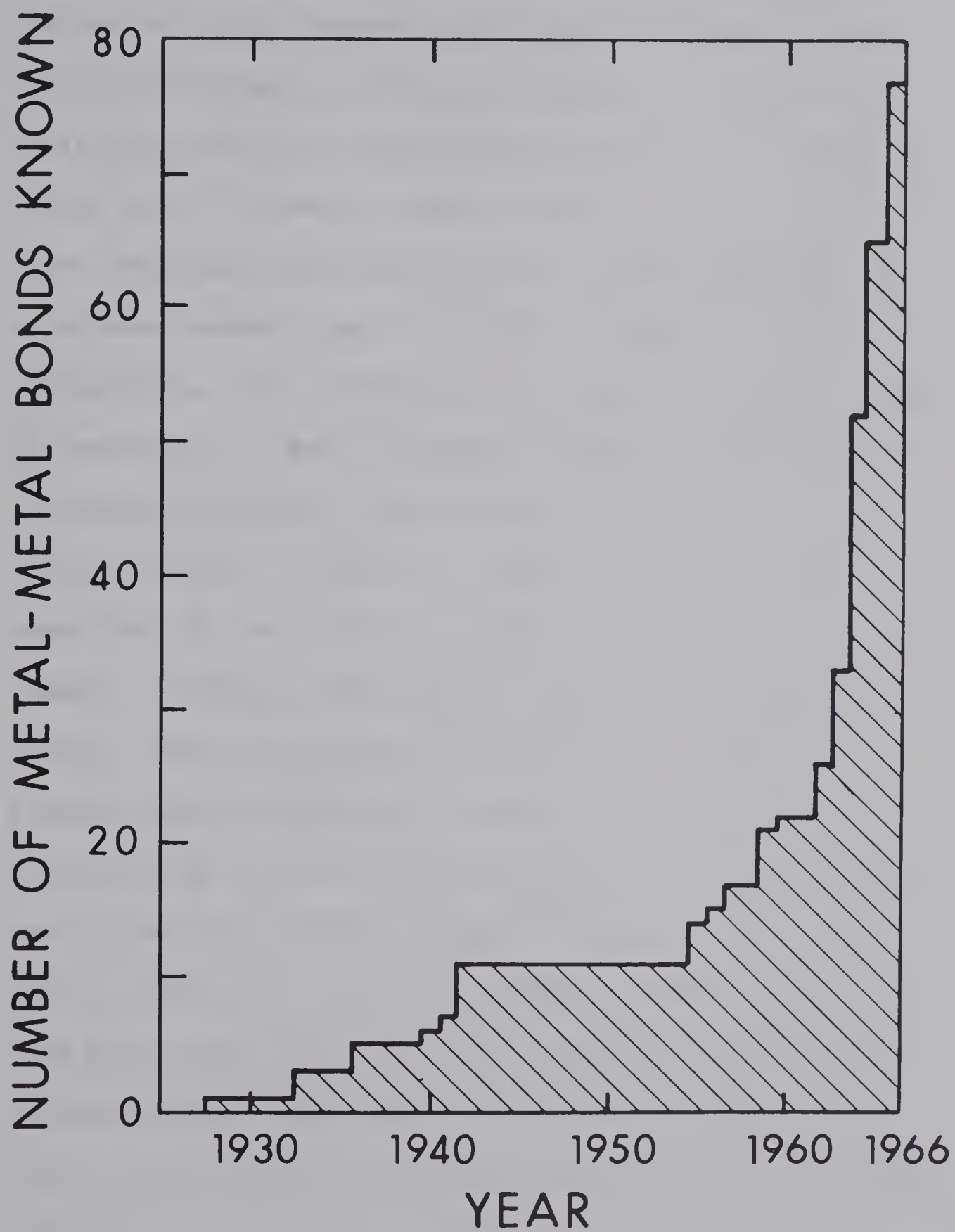


Figure 1

bonds reported up to the end of 1966 (excluding reports of the present work), together with examples, is given in Table I.* Silicon is included in this list, although it is not a metal, as its derivatives are very similar in properties to those of Ge, Sn and Pb. From this table it can be seen that most of the known compounds involve derivatives of group IV, mercury, and to a lesser extent, group I metals. In general metals in the middle of the first transition series form the greatest number of compounds, but this is probably because of unavailability of starting materials, particularly in the case of some of the rarer metals. There is no reason to suppose at this stage that all the metals of groups I to IV inclusive are not capable of forming stable bonds to most of the transition metals. When one considers that the maximum number of possible binary combinations of each of the main group metals Cu, Ag, Au, Zn, Cd, Hg, Ga, In, Tl, Ge, Sn and Pb with each of the 21 transition elements V to Ni, Nb to Pd and Hf to Pt, is 252, and that it is possible to combine one or more main group metals with one or more transition metals, it can be seen that the scope of this field is very large, and that much more work remains to be done in the synthetic field alone.

*In this Table, and throughout this work, the following abbreviations will be employed: Me = CH_3 , Et = C_2H_5 , Bu = $n\text{-C}_4\text{H}_9$, Ph = C_6H_5 , Cp = π bonded cyclopentadienyl group, acac = acetylacetonate, THF = Tetrahydrofuran.

TABLE I

Summary of Known Metal-Metal Bonds

M_T^a	M_M^a	Compound	Ref.	M_T	M_M	Compound	Ref.
V	Cu	$LCuV(CO)_6^b$	15	Mn	Cu	$LCuMn(CO)_5^c$	21
	Au	$Ph_2PAuV(CO)_6$	15	Ag		$LAGMn(CO)_5^b$	21
Ta	Hg	$MeHgTa(CO)_6$	16	Au		$Ph_3PAuMn(CO)_5$	20,22
Cr	Hg	$Hg[Cr(CO)_3Cp]_2$	11	Hg		$Hg[Mn(CO)_5]_2$	23
	Ge	$Ph_3GeCr(CO)_3Cp$	17	Si		$Ph_3SiMn(CO)_5$	24
	Sn	$Ph_3SnCr(CO)_3Cp$	17,18	Ge		$Ph_3GeMn(CO)_5$	25
	Pb	$Ph_3PbCr(CO)_3Cp$	17	Sn		$Me_2Sn[Mn(CO)_5]_2$	14
Mo	Hg	$Hg[Mo(CO)_3Cp]_2$	11	Pb		$Et_3PbMn(CO)_5$	14
	Ge	$Ph_3GeMo(CO)_3Cp$	17	Re	Si	$Ph_3SiRe(CO)_5$	24
	Sn	$Cl_3SnMo(CO)_3Cp$	11	Ge		$Ph_3GeRe(CO)_5$	24
	Pb	$Ph_3PbMo(CO)_3Cp$	18	Sn		$BrSn[Re(CO)_5]_3$	26,27
W	Au	$Ph_3PAuW(CO)_3Cp$	20	Pb		$Ph_3PbRe(CO)_5$	26,27
	Hg	$Hg[W(CO)_3Cp]_2$	11	Fe	Cu	$(LCu)_2Fe(CO)_4^b$	21
	Ge	$Ph_3GeW(CO)_3Cp$	17	Ag		$(LAg)_2Fe(CO)_4^b$	21
	Sn	$Cl_3SnW(CO)_3Cp$	19	Au		$(Ph_3PAu)_2Fe(CO)_4$	20
	Pb	$Ph_3PbW(CO)_3Cp$	17,18	Cd		$[CdFe(CO)_4]_2$	28

^a M_T = Transition Metal, M_M = Main group metal.

^b $L = [(o-Me_2AsC_6H_4)_2AsCH_3]$.

^c $L = CH_3-C(CH_2AsMe_2)_3$

TABLE I (continued)

M_T^a	M_M^a	Compound	Ref.	M_T	M_M	Compound	Ref.
Fe	Hg	$(PhHg)_2Fe(CO)_4$	29	Co	Si	$Cl_3SiCo(CO)_4$	36
	Tl	$Tl_2Fe_3(CO)_{12}$	30		Ge	$Et_3GeCo(CO)_4$	37
	Si	$Me_3SiFe(CO)_2Cp$	31		Sn	$Me_2Sn[Co(CO)_4]_2$	12
	Ge	$Ph_3GeFe(CO)_2Cp$	25		Pb	$Ph_3PbCo(CO)_4$	32
	Sn	$(Ph_3Sn)_2Fe(CO)_4$	32	Rh	Hg	$ClHgRhCl_2L_3^h$	38
	Pb	$(Ph_3Pb)_2Fe(CO)_4$	29		Sn	$Cl_3SnRh(NBD)_2^i$	39
Ru	Hg	$[ClHgRu(CO)_3L_2]M^d$	33	Ir	Au	$Ph_3PAuIr(CO)_3PPh_3$	40
	Sn	$[(Cl_3Sn)_2RuCl_2]M_2^e$	34		Hg	$ClHgIrCl_2(CO)L_2^j$	41
Os	Hg	$[ClHgOs(CO)_3L_2]M^f$	33		Si	$Cl_3IrClH(CO)L_2^k$	42
Co	Cu	$LCuCo(CO)_4^b$	21		Sn	$[(Cl_3Sn)_2IrCl_3]^{2-}$	34
	Ag	$AgCo(CO)_4$	6,7,8			$Cl_3SnIrL_2^l$	39,43
	Au	$Ph_3PAuCo(CO)_4$	20	Pd	Ge	$(Ph_3Ge)_2PdL_2^m$	44
	Zn	$Zn[Co(CO)_4]_2$	9		Sn	$[(Cl_3Sn)_2PdCl]M^n$	45
	Cd	$Cd[Co(CO)_4]_2$	9	Pt	Si	$Me_3SiPtCl(PEt_3)_2$	46
	Hg	$Hg[Co(CO)_4]_2$	9		Ge	$Ph_3GePtH(PEt_3)_2$	47
	In	$In[Co(CO)_4]_3$	9		Sn	$[(Cl_3Sn)_5Pt]M_3^o$	48
	Tl	$Tl[Co(CO)_4]_3$	9			$Cl_3SnPtCl(PPh_3)_2$	48
	Si	$Ph_3SiCo(D_2H_2)Py^g$	35				

^d. L = PPh₃, M = HgCl₃⁻.

^e. M = Et₄N⁺.

^f. L = PPh₃, M = HgCl₃⁻.

^g. D H₂ = Dimethylglyoxime,

Py = Pyridine.

^h. L = Ph₂AsMe.

ⁱ. NBD = Norbornadiene.

^j. L = PPh₃.

^k. L = Ph₂AsMe

^l. L = cycloocta-1,5-diene.

^m. L = PPh₃.

ⁿ. M = Ph₄As⁺.

^o. M = Ph₃PMe⁺.

2. General Discussion

Most of the compounds known at present involve transition metals stabilized in low oxidation states by such ligands as carbon monoxide, tertiary phosphines, and various cyclic olefins such as cyclopentadiene. Examples include $\text{Ph}_3\text{GeMn}(\text{CO})_5$ (25), $\text{Cl}_3\text{SnRh}(\text{PPh}_3)_3$ (39), and $\text{Cl}_3\text{SnIr}(\text{cycloocta-1,5-diene})_2$ (39), and various mixed derivatives such as $\text{Hg}[\text{Mo}(\text{CO})_3\text{Cp}]_2$ (11) and $\text{Me}_2\text{Sn}[\text{Ir}(\text{CO})_3\text{PPh}_3]_2$ (40) where the transition metal is considered to have an oxidation number of -1. There are also a number of ionic species known, such as $[\text{ClHgRu}(\text{CO})_3(\text{PPh}_3)_2]^+$ $[\text{HgCl}_3]^-$ (33), where the oxidation number of the transition metal is 0. A much more extensive list of examples is found in Table I.

In the large majority of metal-metal bonded species involving main and transition metals, the d orbitals of the latter are all completely filled and thus such derivatives do not display properties usually associated with transition metal complexes such as paramagnetism and absorption in the visible region due to d-d transitions. This seems to be true for all compounds of the first transition series, but numerous examples are known of compounds involving second and third transition metals where this is not always true, e.g.

$(\text{Ph}_3\text{Ge})_2\text{Pt}(\text{PEt}_3)_2$ (47) which is a d^8 complex.

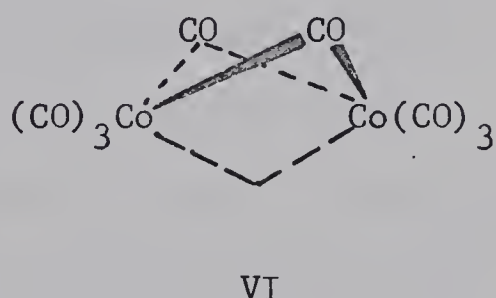
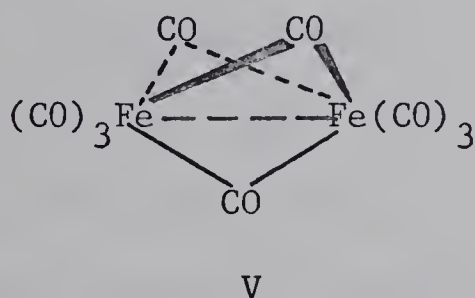
The apparent need for transition metal complexes

involving certain covalently bonded ligands such as CO and C_5H_5 , to completely fill their electron shell, and achieve the electronic configuration of the "inert" gas succeeding it in the periodic table, is usually referred to as the Effective Atomic Number (E.A.N.) rule, or sometimes as the inert gas rule (49). In order to determine whether or not a particular compound obeys this rule, the electrons in the valence shell are counted. If the transition metal is taken to be in the zero oxidation state, then the following numbers of electrons have to be supplied by the groups bonded to it:

No. of electrons needed:	13	12	11	10	9	8	0
	V	Cr	Mn	Fe	Co	Ni	Kr
	Nb	Mo	Tc	Ru	Rh	Pd	Xe
	Ta	W	Re	Os	Ir	Pt	Rn

When counting the number of electrons supplied, ligands such as CO and phosphines are considered to supply two; halogens, main group metals and other groups that form covalent electron pair bonds supply one, while the π -bonded cyclopentadienyl group (C_5H_5) supplies five. In the case of $Me_3SnCo(CO)_4$, for example, the four CO groups supply a total of 8 electrons, while the Me_3Sn group supplies one, making a total of nine, the compound

thus obeys the E.A.N. rule. This is true of all tetracarbonyl-cobalt derivatives. Compounds obeying the EAN rule are diamagnetic. As there are quite a number of metal carbonyl derivatives which do not obey this rule, e.g. the paramagnetic vanadium hexacarbonyl, this concept is not to be regarded as inviolable, although it often proves to be a useful principle when postulating possible structures for new compounds. In particular this rule has been invoked in explaining the diamagnetism of various binuclear carbonyls which possess carbonyl bridges, such as $\text{Fe}_2(\text{CO})_9$ (V), $[\text{Fe}(\text{CO})_2\text{Cp}]_2$ and $\text{Co}_2(\text{CO})_8$ (VI).

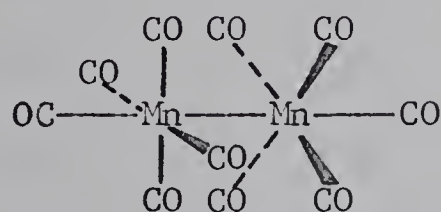


The structures of these compounds were determined by X-ray methods (50,51,52), but from these it was not possible to conclude that the transition metals were directly bonded to each other. However, if direct metal-metal bonding was absent from these compounds, then each metal atom would be one electron short of the inert gas configuration, and thus possess an unpaired electron which would result in paramagnetism. Their observed diamagnetism is therefore explained in terms of metal-metal bonds which results in coupling of the two unpaired electrons, and allows each metal to achieve the

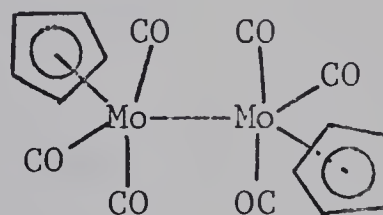
electronic configuration of the next inert gas. It is possible that the diamagnetism is due to coupling of the unpaired electrons via the bridging CO groups, and not to an actual metal-metal bond, as pointed out by Orgel (53) for $\text{Fe}_2(\text{CO})_9$. However, structural determinations of a number of bridged species carried out by Dahl and co-workers have pointed very strongly to metal-metal bonds. For instance, the structures of sulphur bridged iron carbonyls such as $[\text{EtSFe}(\text{CO})_3]_2$ (54) and $[\text{SFe}(\text{CO})_3]_2$ (55) possess non-planar Fe_2S_2 fragments with remarkably acute Fe-S-Fe angles of 68° and 70° respectively. This, the authors suggest, is due to "the energy gained from attainment of better overlap of the two iron orbitals with each other", resulting in a 'bent' iron-iron bond, the overlapping orbitals not being colinear with the line through the two iron atoms. An even more dramatic illustration is given by the structures of $(\text{Ph}_2\text{PCoCp})_2$ and $(\text{Ph}_2\text{PNiCp})_2$ (56). In the former compound the EAN rule requires a Co-Co bond, and the Co_2P_2 ring is in fact nonplanar with a Co-P-Co angle of 73° , and a bonding Co-Co distance of 2.56Å. The latter compound, however, does not require a Ni-Ni bond, and in fact the Ni_2P_2 ring is planar with a normal symmetrically bridging Ni-P-Ni angle of 103° , and a non-bonding $\text{Ni}\cdots\text{Ni}$ distance of 3.36Å. If coupling of the unpaired electrons across the bridging phosphorous were taking place in the cobalt derivatives it would be

expected to have a similar structure to the planar nickel compound. On the above evidence it seems very reasonable to postulate similar 'bent' metal-metal bonds in $[\text{Fe}(\text{CO})_2\text{Cp}]_2$ and $\text{Co}_2(\text{CO})_8$.

The first reports of structures which showed unambiguously the existence of bonds between transition metals appeared in 1957. In that year the structures of both $\text{Mn}_2(\text{CO})_{10}$ (57), and $[\text{Mo}(\text{CO})_3\text{Cp}]_2$ (58) were reported, and both were shown to possess non-bridged Mn-Mn and Mo-Mo bonds respectively (VII and VIII).

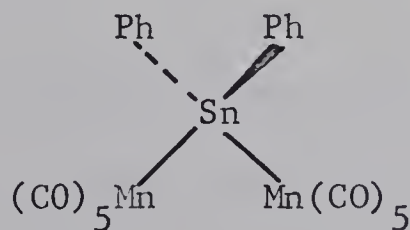


VII



VIII

It was not until 1964, however, that the existence of main to transition metal bonds was proved by X-ray structural determinations. In that year the structures of both $\text{Ph}_3\text{SnMn}(\text{CO})_4\text{PPh}_3$ (54), and $\text{Ph}_2\text{Sn}[\text{Mn}(\text{CO})_5]_2$ (60), (IX), were reported.



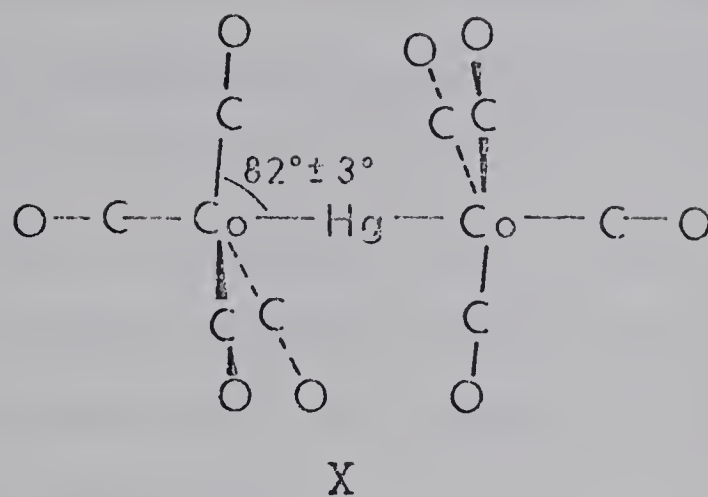
IX

Since that time an increasing number of X-ray structures of such derivatives have been carried out. Table II gives examples of these, together with metal-metal bond lengths.

TABLE II

Bond	Bond length A.	Compound	Reference
Mo-Sn	2.85	$\text{Ph}_3\text{SnMo}(\text{CO})_3\text{Cp}$	18
Mn-Cu	2.56	$(\text{o-Triars})\text{CuMn}(\text{CO})_5$	61
Mn-Ge	2.535	$\text{Ph}_3\text{GeMn}(\text{CO})_5$	61
Mn-Sn	2.675	$\text{Ph}_3\text{Mn}(\text{CO})_5$	62
Fe-Hg	2.44, 2.59	$(\text{BrHg})_2\text{Fe}(\text{CO})_4$	4
Fe-Ge	2.35	$\text{Cl}_2\text{Ge}[\text{Fe}(\text{CO})_2\text{Cp}]_2$	63
Fe-Sn	2.53	$\text{Ph}_3\text{SnFe}(\text{CO})_2\text{Cp}$	64
Co-Au	2.50	$(\text{Ph}_3\text{P})_3\text{AuCo}(\text{CO})_4$	61
Co-Zn	2.305	$\text{Zn}[\text{Co}(\text{CO})_4]_2$	65
Co-Hg	2.497	$\text{Hg}[\text{Co}(\text{CO})_4]_2$	8
Co-Hg	2.56	$(\text{Fe}(\text{CO})_2\text{Cp})\text{HgCo}(\text{CO})_4$	66
Co-Sn	2.66	$[\text{Mn}(\text{CO})_5]\text{Ph}_2\text{SnCo}(\text{CO})_4$	67
Co-Si	2.254	$\text{Cl}_3\text{SiCo}(\text{CO})_4$	68
Ir-Sn	2.642	$\text{Cl}_3\text{SnIr}(\text{C}_8\text{H}_{12})_2$	69

All of the tetracarbonylcobalt derivatives so far reported are listed in this table, while X shows the structure of $\text{Hg}[\text{Co}(\text{CO})_4]_2$.



In the structures of all $\text{Co}(\text{CO})_4$ derivatives, the cobalt is at the centre of a distorted trigonal bipyramid with 3 equatorial CO groups and one axial CO group, the main group metal taking up the other axial position. In each case the equatorial carbonyl groups are bent out of the plane towards the metal so that the C-Co-M angle is typically in the range 85° to 82° . This has also been observed for various $\text{Mn}(\text{CO})_5$ derivatives where the four equatorial CO groups are again bent towards the metal. It is possible that this distortion is caused by repulsions between the π bonds at the axial and equatorial groups. However Manning and Miller (70) discussed the possibility of enhanced Mn-Co π bonding when the equatorial groups are distorted out of the plane, suggesting that such distortion allows $d \rightarrow \pi^*$ overlaps not allowed in the strictly non-distorted structure.

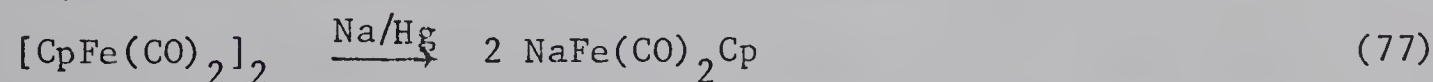
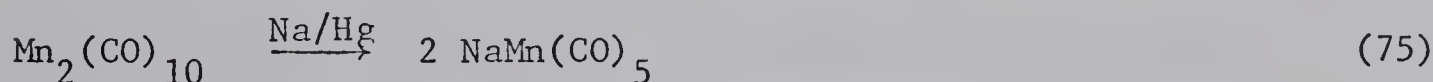
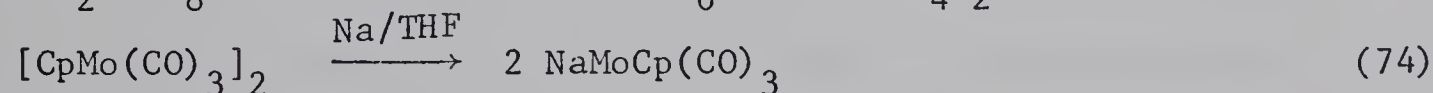
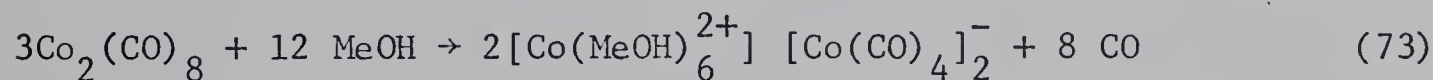
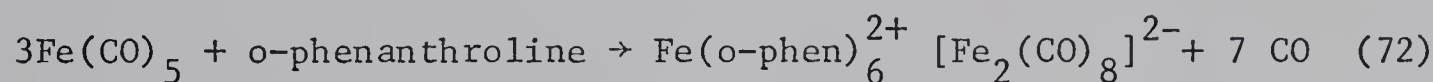
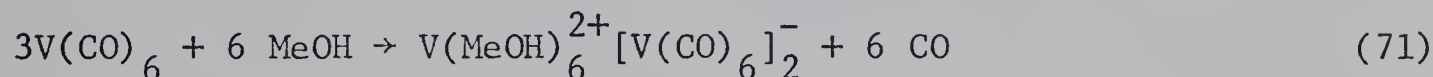
3. Summary of Synthetic Methods.

The following short summary lists the more common methods by which metal-metal bonded compounds have been synthesized.

a) Displacement of Halide ions by Metal Carbonyl Anions

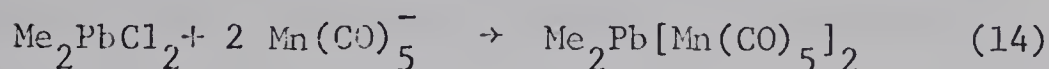
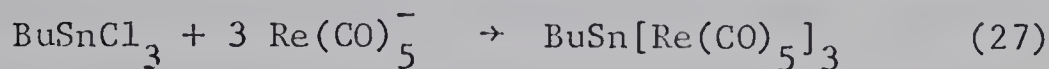
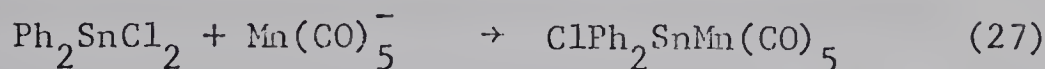
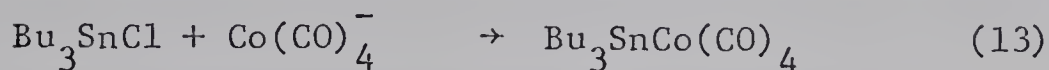
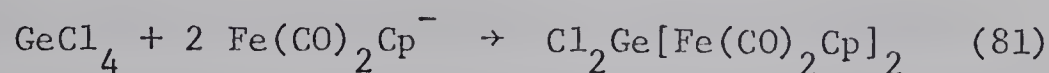
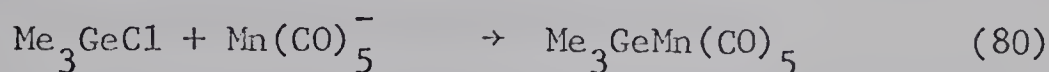
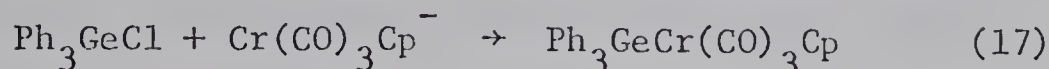
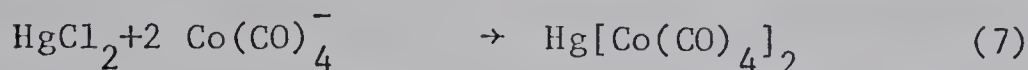
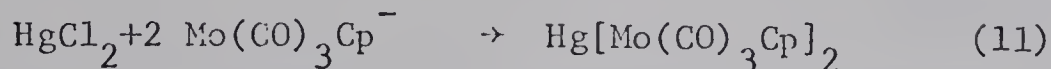
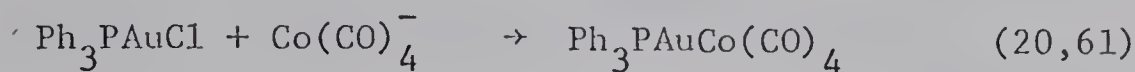
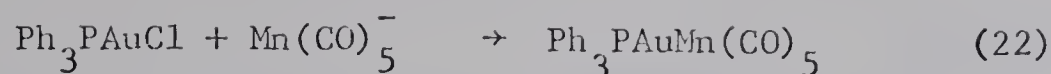
Anionic metal carbonyl species are known for many transition metals e.g. $\text{Co}(\text{CO})_4^-$ and $\text{Mn}(\text{CO})_5^-$, and are mostly prepared by either action of base on a neutral carbonyl species, or by reduction of the latter with, for instance, sodium amalgam.

Examples of such reactions are:



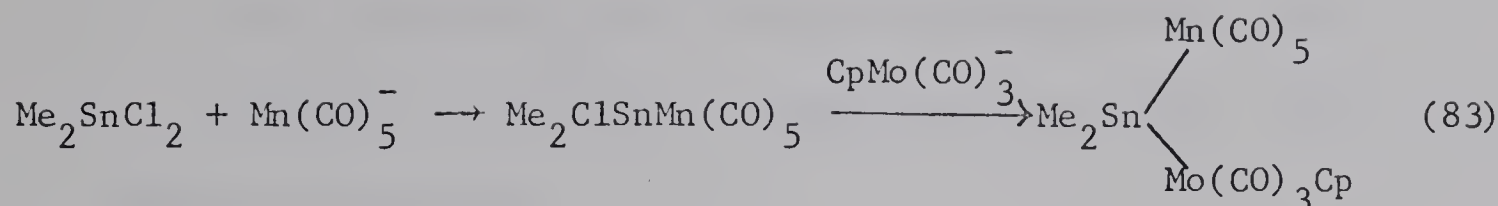
A detailed description of the preparation and reaction of such anionic species is given in a review by King (79).

When metal carbonyl anions are allowed to react with organometallic halides, replacement of halide ion by the anion occurs giving a compound with a metal-metal bond, as illustrated by the following examples:



If the organometal halide possesses more than one halogen, it is usually possible to control the degree of substitution by varying the ratio of reactants. For example, Me_2SnCl_2 reacts with one mole of $\text{Mo}(\text{CO})_3\text{Cp}^-$ to give $\text{ClMe}_2\text{SnMo}(\text{CO})_3\text{Cp}$, while two moles of anion affords $\text{Me}_2\text{Sn}[\text{Mo}(\text{CO})_3\text{Cp}]_2$ (17). Using these methods it has been possible to attach three, and in some cases four, transition metals to tin, thus treatment of BuSnCl_3 with three moles of $\text{Re}(\text{CO})_5^-$ afforded $\text{BuSn}[\text{Re}(\text{CO})_5]_3$ (27), while SnCl_4 reacted with four moles of $\text{Fe}(\text{CO})_2\text{Cp}^-$ to give $\text{Sn}[\text{Fe}(\text{CO})_2\text{Cp}]_4$ (82).

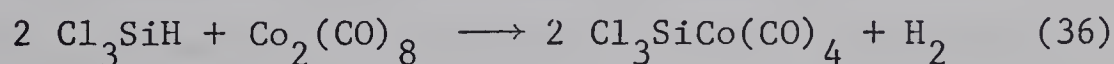
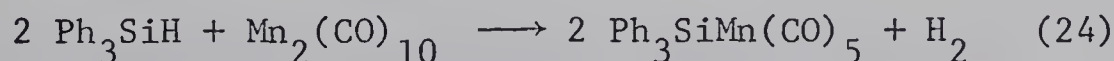
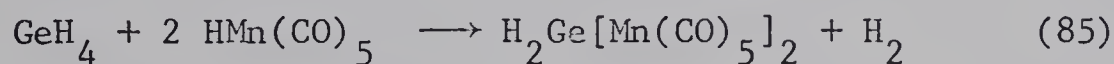
Compounds with two or more different transition metals bonded to one main group metal can be prepared by stepwise replacement of halide ion with two or more different anions, e.g.:



Anion replacement reactions are the most frequently employed methods used for synthesizing metal-metal bonds.

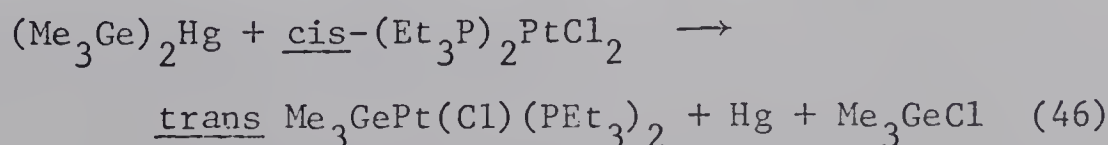
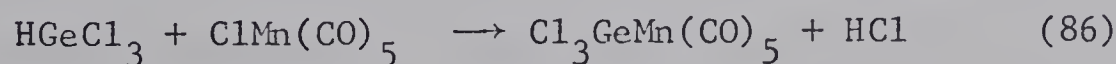
b) Reactions Involving Elimination of a Neutral Molecule

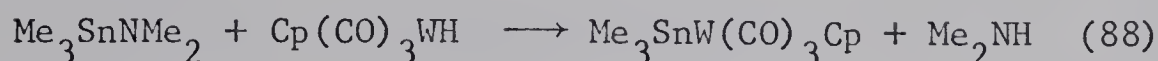
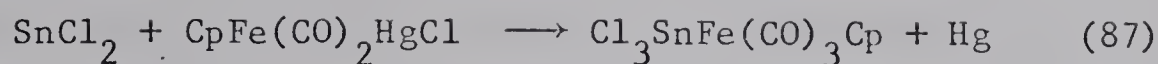
There are numerous reports of reactions between transition and main group derivatives which involve elimination of a neutral molecule and formation of metal-metal bonds. Many of these reactions involve main group hydrides and transition metal carbonyl derivatives, e.g.:



These reactions are believed to involve two stages. In the first stage one mole of hydride, e.g. Cl_3SiH , reacts with one mole of, say, $\text{Co}_2(\text{CO})_8$ giving $\text{Cl}_3\text{SiCo}(\text{CO})_4$ and $\text{HCo}(\text{CO})_4$, the latter then reacts with more Cl_3SiH affording more $\text{Cl}_3\text{SiCo}(\text{CO})_4$ and H_2 (36).

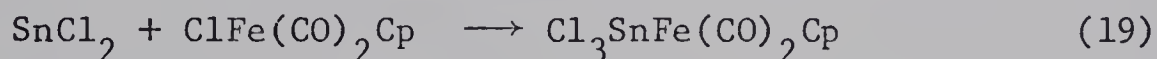
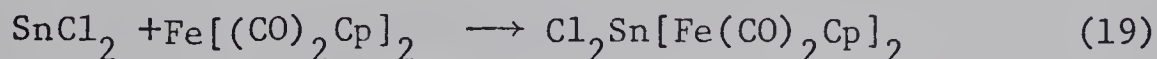
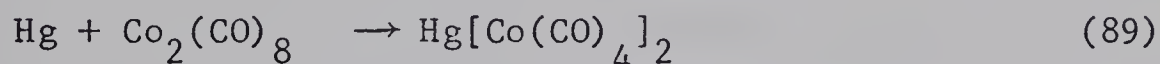
Examples of reactions in which other molecules are eliminated include:





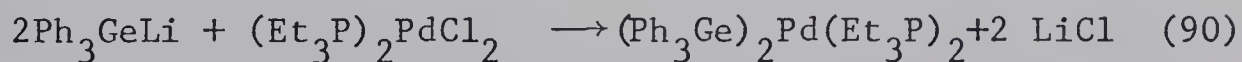
c) Insertion Reactions

These involve the reaction of main group derivatives in their lower oxidation, such as Hg and SnCl_2 , with either dimeric transition metal carbonyl derivatives, or transition metal halide complexes, and results in insertion of the main group metal into either the metal-metal or the metal-halogen bonds. These reactions are discussed in more detail in chapter IV. Examples of this type of reaction are:



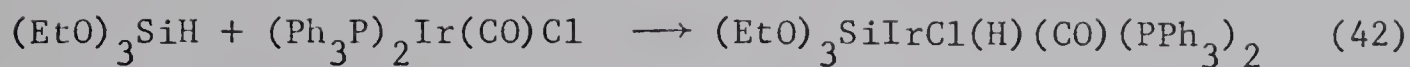
d) Halide Displacement by Group IV Lithium Derivatives

This method involves reaction of such compounds as Ph_3GeLi with transition halide complexes, and has been used largely to prepare germanium and tin derivatives of platinum and palladium e.g.:



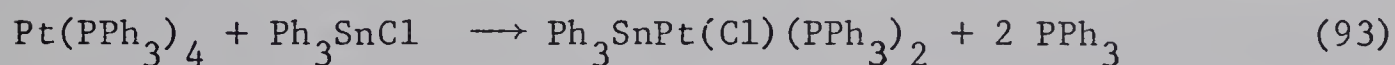
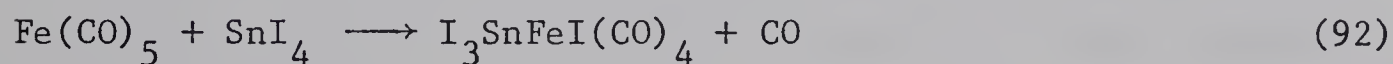
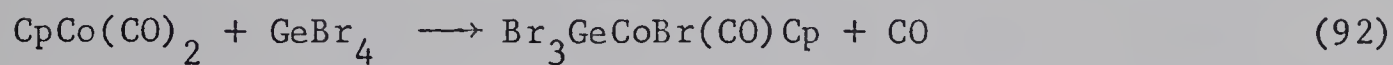
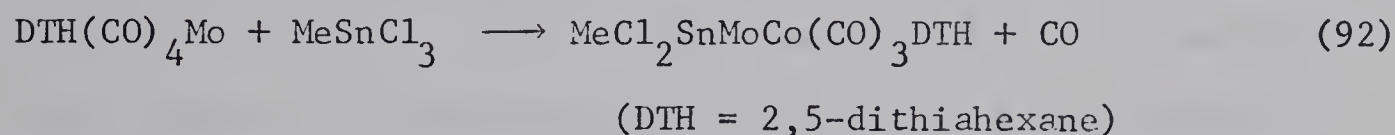
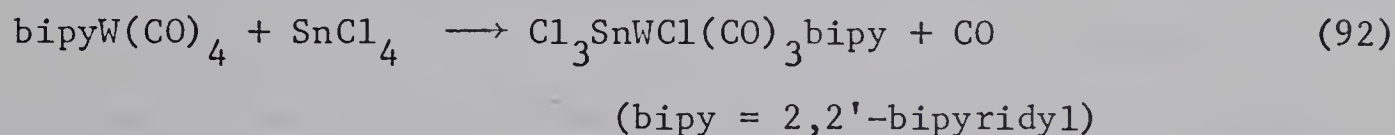
e) Oxidative-Addition Reactions

In these reactions a four or five coordinate transition metal complex adds a molecule of a main group derivative to form a complex in which the transition metal has increased its oxidation state by two units, e.g.:



f) Oxidative-Elimination Reactions

Reactions of this type involve attack of a transition metal complex by main group halides with oxidation of the transition metal, and elimination of a ligand such as CO and PPh_3 , e.g.:



In the first two examples the products involve 7-coordinate W and Mo.

Of the six methods outlined above, the first, involving anion displacement reactions, has been used to a greater extent for preparing tetracarbonylcobalt derivatives, although a number of derivatives were made by high pressure reactions of CO with CoBr_2 and a main group metal (9), as mentioned earlier.

CHAPTER II

The Synthesis of Tetracarbonylcobalt Derivatives of Germanium and Tin

INTRODUCTION

The first tetracarbonylcobalt derivative of a group IV metal was reported in 1942 by Hieber and Teller (9) who prepared a substance formulated as $\text{Sn}[\text{Co}(\text{CO})_4]_2$ by a high pressure synthesis from CoBr_2 , tin metal and carbon monoxide at several hundred atmospheres. Later, Hieber and Breu (13) reported the preparation of $\text{R}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$, ($\text{R} = \text{Me}$ or Bu) and $\text{Bu}_3\text{SnCo}(\text{CO})_4$ by reaction of cobalt carbonyl anion with organotin halides in methanol solution. At the time the nature of these compounds was not known and the authors postulated the presence of carbonyl bridges between tin and cobalt, as discussed in Chapter I, instead of tin-cobalt bonds which is now known to be the case. In 1957 Hein et al. (32) reported the preparation of lead derivatives such as $\text{Ph}_3\text{PbCo}(\text{CO})_4$ by the action of $\text{NaCo}(\text{CO})_4$ on Ph_3PbOH .

After the commencement of the present work, a number of papers appeared which described the preparation of some tetracarbonylcobalt derivatives of group IV metals. The germanium derivative $\text{Et}_3\text{GeCo}(\text{CO})_4$ was prepared by Kahn and Bigorgne (37) by the reaction of Et_3GeH with $\text{Co}_2(\text{CO})_8$, while

anion displacement reactions were employed by Hein and Jehn (94) to prepare the tin and lead derivatives $\text{Ph}_3\text{SnCo}(\text{CO})_4$, $\text{Ph}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$, $(\text{C}_6\text{H}_{11})_3\text{PbCo}(\text{CO})_4$ and $\text{Ph}_2\text{Pb}[\text{Co}(\text{CO})_4]_2$. Some mixed derivatives of tin have also recently been prepared in which two different transition metals are bonded to tin; thus Nesmeyanov et al. (95) reported $\text{Ph}_2\text{Sn}[\text{Co}(\text{CO})_4][\text{Mn}(\text{CO})_5]$ and $\text{PhClSn}[\text{Co}(\text{CO})_4][\text{Mn}(\text{CO})_5]$, both prepared by anion replacement reactions.

Silicon also forms stable bonds to cobalt, a number of $\text{R}_3\text{SiCo}(\text{CO})_4$ derivatives having been prepared by Chalk and Harrod (36) by reactions of R_3SiH with $\text{Co}_2(\text{CO})_8$ where $\text{R}_3 = \text{Et}_3$, Ph_3 , $(\text{MeO})_3$, PhCl_2 and Cl_3 , while silylcobalt tetracarbonyl itself ($\text{H}_3\text{SiCo}(\text{CO})_4$) was made by Aylett and Campbell (96) from H_3SiI and $\text{NaCo}(\text{CO})_4$.

Schrauzer and Kratel (35) have recently reported some novel group IV derivatives of cobalt in which dimethylglyoxime, rather than CO, is coordinated to cobalt. They have prepared $\text{Ph}_3\text{MCo}(\text{D}_2\text{H}_2)\text{Py}$ (where $\text{M} = \text{Si}, \text{Ge}, \text{Sn}$ and Pb , $\text{D} =$ the dianion of dimethylglyoxime, and $\text{Py} =$ pyridine) as stable crystalline materials.

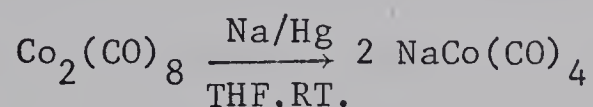
Although one germanium and numerous tin derivatives were known (as detailed above), no previous attempt has been made to study such derivatives systematically. It was with this end in view that a detailed synthetic study of a series of tetracarbonylcobalt derivatives of germanium and tin was undertaken.

RESULTS AND DISCUSSION

1. General Procedures

Many of the germanium and tin compounds discussed in this chapter were prepared by displacement of halide ion from an organometal halide by the tetracarbonylcobaltate(-1) ion ($\text{Co}(\text{CO})_4^-$). The latter was conveniently prepared by one of two methods:

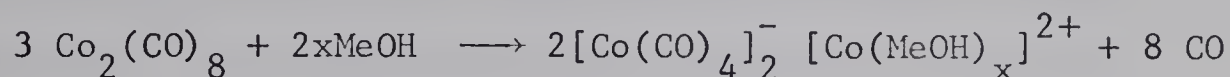
a) Reduction of $\text{Co}_2(\text{CO})_8$ by Sodium Amalgam. In this method a solution of $\text{Co}_2(\text{CO})_8$ in tetrahydrofuran (THF) was stirred with excess of 1% sodium amalgam for about 30 minutes. At the end of this period the solution had lost its original red colour and became pale yellow, or sometimes grey due to suspended mercury (78):



The solution contains $\text{NaCo}(\text{CO})_4$ contaminated with a small percentage of $\text{Hg}[\text{Co}(\text{CO})_4]_2$. It was suggested by Dighe and Orchin (97) that reduction of $\text{Co}_2(\text{CO})_8$ proceeds via the initial formation of $\text{Hg}[\text{Co}(\text{CO})_4]_2$ which reacts further with Na to give $\text{NaCo}(\text{CO})_4$ and Hg. This would explain the presence of the mercury derivative in solutions of $\text{NaCo}(\text{CO})_4$ prepared by this method. Because of this impurity, a 5-10% excess of $\text{Co}_2(\text{CO})_8$ was usually employed; however in none of the reactions carried out were the products contaminated with $\text{Hg}[\text{Co}(\text{CO})_4]_2$.

b) Reaction of $\text{Co}_2(\text{CO})_8$ with Methanol. This method could only be used if the metal halide did not react with methanol.

The $\text{Co}(\text{CO})_4^-$ anion was generated in this solvent by heating a methanol solution of $\text{Co}_2(\text{CO})_8$ to about 50° until CO evolution had ceased and the solution had turned pale red (73).



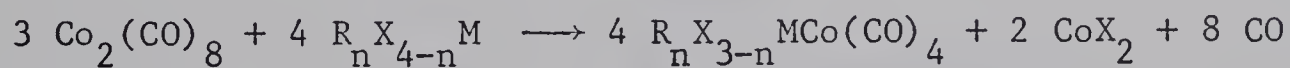
The quantity of $\text{Co}_2(\text{CO})_8$ required was calculated from the above equation, three moles of cobalt carbonyl producing 4 moles of $\text{Co}(\text{CO})_4^-$. The disadvantage of this procedure is that only 2/3 of $\text{Co}_2(\text{CO})_8$ is converted to the anion, the remainder is oxidised to Co^{2+} . However this method is more convenient and more rapid than sodium amalgam reduction of cobalt carbonyl.

The preparation of $\text{Co}(\text{CO})_4^-$, and its subsequent reactions, were always carried out in a nitrogen atmosphere because of the rapidity with which the anion undergoes atmospheric oxidation.

Reaction with organometal halide, in either THF or methanol, was carried out by mixing solutions of stoichiometric quantities of anion and halide together in the same solvent, and stirring at room temperature for 10 to 15 minutes to ensure that the reaction was complete. The method used to work up the reaction mixture depended upon the solvent which was used. Methanol solutions were first filtered and cooled in ice, after which distilled water was added slowly. The product would usually come down as a reasonably pure crystalline precipitate which was then dried in vacuo. If greater purity was required, the product was recrystallized from n-pentane by cooling a

saturated solution to about -20° . If THF was used as solvent, the reaction mixture was worked up by evaporating the solvent at room temperature under reduced pressure using a rotary evaporator. The residue from this evaporation was then extracted with several portions of n-pentane, the extracts combined, filtered, and evaporated under reduced pressure to a small volume or until crystals began to form. The solution was then cooled to about -20° to complete crystallization. The product was then usually recrystallized from n-pentane.

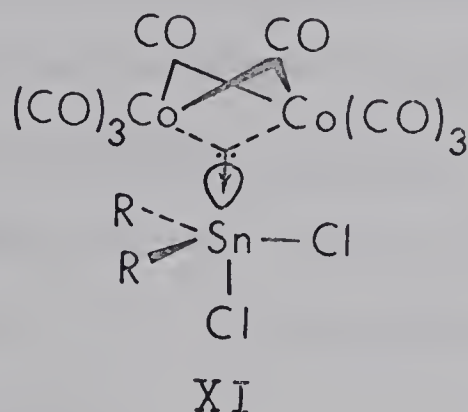
The other important procedure employed to prepare tetracarbonylcobalt derivatives of tin and germanium involved the reaction of $\text{Co}_2(\text{CO})_8$ itself with either an organometal halide or tetrahalide. By varying the ratios of the two reactants and choosing suitable solvents, compounds with one, two, three and four tetracarbonylcobalt groups attached to the central group IV metal could be prepared, e.g.:



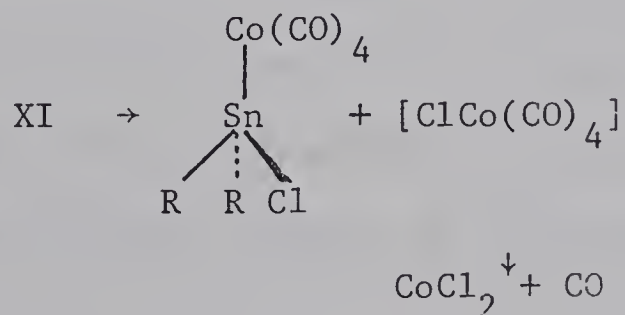
In these reactions 1/3 of the cobalt atoms are oxidised to Co (II) compounds, and CO is evolved. The reaction is slower than the anion replacement reactions described above, and can be followed by the CO evolution, cessation of which indicates that reaction is complete.

The mechanism of this reaction is obscure. It may perhaps proceed via interaction of the cobalt-cobalt bond with tin giving an unstable intermediate adduct in which the tin is

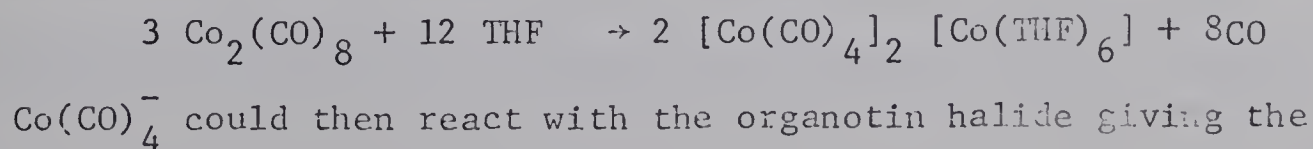
essentially 5-coordinate. This would be similar to the stable adduct formed between $\text{Co}_2(\text{CO})_8$ and AlBr_3 (98) in which the bent Co-Co bond is believed to donate into an empty Al orbital. Such an adduct of an organotin halide would have a structure such as that shown in XI.



This could then rearrange with Co-Co and Sn-Cl bond fission giving $\text{R}_2\text{ClSnCo}(\text{CO})_4$ and $\text{ClCo}(\text{CO})_4$, the latter, being unstable, would then decompose into CoCl_2 and CO.



A second possible reaction mechanism in THF solution would involve interaction of THF with $\text{Co}_2(\text{CO})_8$ causing disproportionation and formation of $\text{Co}(\text{CO})_4^-$ and Co^{2+} :



observed product.

2. Synthesis of Germanium Derivatives

Compounds with one or two tetracarbonylcobalt groups bonded to germanium were prepared, their analytical data, colours and melting points being given in Table III.

Spectroscopic studies are described in detail in Chapter V.

(i) Mono(tetracarbonylcobalt) Derivatives - These were mostly prepared by anion displacement reactions involving treatment of equimolar quantities of an organogermanium halide with Co(CO)_4^- in THF solution:



$$n = 0, \text{ X} = \text{Cl}$$

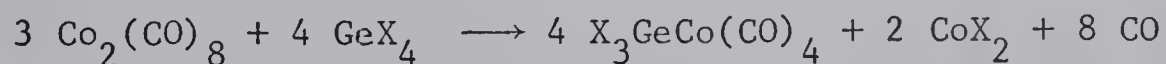
$$n = 1, \text{ R} = \text{Ph, and X} = \text{Cl}$$

$$\text{R} = \text{Me, and X} = \text{I}$$

$$n = 2, \text{ R} = \text{Ph, Me, and X} = \text{Cl}$$

The triphenyl derivative however, was made in methanol solution.

The trihalo-derivatives were also prepared by action of a germanium tetrahalide on cobalt carbonyl in THF solution at room temperature:



$$\text{X} = \text{Cl, Br, I}$$

The reaction was complete in 5-15 minutes, and the reaction mixture was worked up by evaporation of solvent and extraction

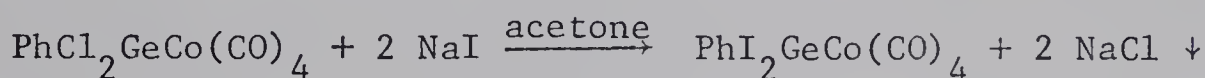
TABLE III

Analytical Data, Colours and Melting Points for Germanium Derivatives

Compound	M.p., °C	Colour	Calculated %			Found %				
			C	H	O	X	C	H	O	X
Cl ₃ GeCo(CO) ₄	71-73	Yellow	13.7	0.0	-	30.4	14.2	0.2	-	27.0
Cl ₂ PhGeCo(CO) ₄	59-61	Pale Yellow	30.9	1.3	16.3	18.1	31.1	1.4	16.0	14.3
ClPh ₂ GeCo(CO) ₄	59-61	Pale Yellow	44.2	2.3	-	8.2	44.2	2.3	-	7.0
ClMe ₂ GeCo(CO) ₄	51-54	Pale Yellow	23.3	2.0	-	11.5	21.6	1.9	-	12.7
Br ₃ GeCo(CO) ₄	dec 102	Yellow	9.9	0.0	-	49.5	9.9	0.0	-	45.3
I ₃ GeCo(CO) ₄	dec 110	Orange	7.7	0.0	-	61.0	9.1	0.0	-	62.9
I ₂ MeGeCo(CO) ₄	70-72	Yellow	11.7	0.6	-	49.5	11.8	0.8	-	51.4
Ph ₃ GeCo(CO) ₄	130	White	55.7	3.2	-	-	57.2	3.1	-	-
Cl ₂ Ge[Co(CO) ₄] ₂	102-104	Red	19.8	0.0	26.5	14.6	20.0	0.0	26.6	14.5
IMeGe[Co(CO) ₄] ₂	66-68	Orange	19.4	0.5	23.0	22.8	20.9	0.2	22.2	25.2
Me ₂ Ge[Co(CO) ₄] ₂	39-41	Yellow	27.0	1.4	-	-	26.1	1.5	-	-

of the residue with n-pentane. Evaporation of the extract to a small volume followed by cooling afforded crystals of product.

By treatment of either the phenyldichloro- or the diphenylchlorogermanium derivative with NaI in acetone solution, the corresponding iodo compounds were prepared:



All the mono(tetracarbonylcobalt) derivatives prepared formed white to orange crystals, soluble in both polar and non-polar solvents. They are all somewhat air sensitive, but could be handled in air for short periods of time without any apparent sign of oxidation. However, prolonged exposure to air over periods of many weeks eventually resulted in oxidation. They all possess moderate thermal stabilities, decomposing only above about 100°.

(ii) Bis(tetracarbonylcobalt) Derivatives - Displacement of two halide ions by Co(CO)_4^- was possible for GeCl_4 , MeGeI_3 and Me_2GeCl_2 , however, excess of anion would only replace one Cl^- from Ph_2GeCl_2 , affording $\text{Ph}_2\text{ClGeCo(CO)}_4$.



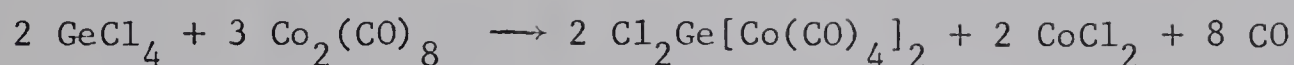
$$n = 0, \text{ X} = \text{Cl}$$

$$n = 1, \text{ X} = \text{Cl}, \text{ I}$$

$$n = 2$$

The dichloro derivative was also prepared by treating GeCl_4

with excess $\text{Co}_2(\text{CO})_8$:



The bis derivatives were yellow to red crystalline materials and were moderately air sensitive, but could be handled in air for short periods without noticeable decomposition.

Attempts to replace more than two halide ions, by treating GeCl_4 or MeGeI_3 with excess $\text{Co}(\text{CO})_4^-$, did not succeed, disubstitution occurring in both cases. This is somewhat surprising considering that both three and four halide ions can be displaced from tin halides by $\text{Co}(\text{CO})_4^-$. This may be due to the higher electronegativity of germanium lowering the polarity of the Ge-X bond thus making displacement of X^- from germanium more difficult. It is also possible that, owing to the smaller size of germanium, there is too much crowding about this atom when two $\text{Co}(\text{CO})_4^-$ groups are attached, for a third $\text{Co}(\text{CO})_4^-$ to approach close enough to react.

3. Synthesis of Tin Derivatives

The tetracarbonylcobalt derivatives of tin described in this chapter are listed in Table IV, together with melting points, colours and analytical data. By means of anion displacement reactions and treatment of organotin halides with $\text{Co}_2(\text{CO})_8$ it was possible to prepare the complete series

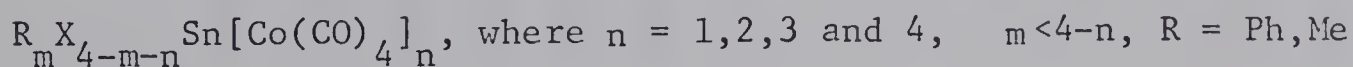


TABLE IV

Analytical Data, Colours and Melting Points of Tin Derivatives

Compound	M.p. °C	Colour	Calculated %			Found %				
			C	H	O	X	C	H	O	X
Cl ₃ SnCo(CO) ₄	79-80	Yellow	12.1	0.0	16.1	26.8	13.2	0.0	15.8	26.4
Cl ₂ PhSnCo(CO) ₄	63-65	Yellow	27.7	1.1	14.6	16.2	27.0	1.1	14.9	13.5
Cl ₂ BuSnCo(CO) ₄	liquid	Orange	23.0	2.2	15.3	17.0	22.9	2.1	15.3	16.8
ClPh ₂ SnCo(CO) ₄	66-68	Yellow	40.5	2.1	13.4	7.4	40.8	2.3	12.8	5.6
ClMe ₂ SnCo(CO) ₄	70-73	White	20.3	1.7	18.0	10.0	20.1	1.7	17.9	9.9
Br ₃ SnCo(CO) ₄	dec 90	Orange	9.2	0.0	12.1	45.3	9.3	0.0	12.1	40.6
Br ₂ PhSnCo(CO) ₄	73-75	Yellow	22.8	0.9	12.1	30.3	23.1	0.8	12.1	30.3
BrPh ₂ SnCo(CO) ₄	55-57	Yellow	36.8	1.9	12.2	15.3	37.1	2.2	12.3	15.6
I ₃ SnCo(CO) ₄	dec 92	Red	7.2	0.0	9.5	56.8	7.4	0.0	9.6	61.8
IPh ₂ SnCo(CO) ₄	69-70	Yellow	33.7	1.8	11.2	22.2	33.6	1.8	11.2	22.5
Ph ₃ SnCo(CO) ₄ ^a	dec 110	White	50.6	2.9	-	0.0	49.8	2.1	-	0.0
Me ₃ SnCo(CO) ₄	73-75	White	25.1	2.7	-	-	25.2	3.3	-	-
Cl(acac) ₂ SnCo(CO) ₄	109-110	Yellow	32.1	2.7	24.5	6.8	31.4	2.9	25.7	5.0

TABLE IV (continued)

Compound	M.p. °C	Colour	Calculated %			Found %				
			C	H	O	X	C	H	O	X
Br ₃ SnCo(CO) ₃ PPh ₃	Dec 135	Orange	33.1	2.0	-	31.4	34.9	2.4	-	30.4
Cl ₂ PhSnCo(CO) ₃ PPh ₃	Dec 158	Yellow	51.2	3.0	-	10.5	47.9	3.1	-	10.3
Cl ₂ BuSnCo(CO) ₃ PPh ₃ ^b	dec 161	Yellow	46.1	3.7	-	10.9	45.9	3.8	-	12.5
ClMeSn[Co(CO) ₄] ₂	---	Yellow	21.1	0.6	-	6.9	20.7	0.8	-	7.0
ClPhSn[Co(CO) ₄] ₂	71-73	Yellow	29.4	0.9	-	6.2	28.9	2.0	-	6.7
ClBuSn[Co(CO) ₄] ₂	29-30	Yellow	26.1	1.6	23.2	6.4	25.9	1.5	22.2	5.4
ClVnSn[Co(CO) ₄] ₂ ^c	45-47	Yellow	23.2	0.6	24.5	6.8	22.7	0.6	23.9	7.5
Me ₂ Sn[Co(CO) ₄] ₂	35-37	Yellow	24.5	1.2	-	0.0	24.3	1.8	-	0.0
Ph ₂ Sn[Co(CO) ₄] ₂	dec 128	Yellow	39.1	1.6	-	0.0	39.0	2.0	-	0.0
(acac) ₂ Sn[Co(CO) ₄] ₂	dec 88	Orange	32.8	2.1	29.1	-	32.8	2.2	28.8	-
(acac) ₂ SnCo ₂ (CO) ₇	dec 86	Red	32.4	2.2	27.9	-	32.9	2.2	27.3	-
ClSn[Co(CO) ₄] ₃ ^d	98-100	Dark red	21.6	-	28.8	5.3	21.1	-	24.4	5.2
BrSn[Co(CO) ₄] ₃ ^e	100-103	Dark red	20.2	0.0	27.0	11.2	20.3	0.0	27.1	10.0
ISn[Co(CO) ₄] ₃	dec 110	Dark purple	19.0	0.0	25.3	16.7	21.4	0.0	26.6	15.9

TABLE IV (continued)

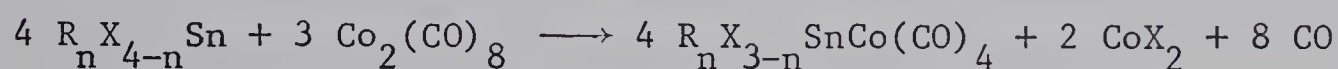
Compound	M.p. °C	Colour	Calculated %			Found %				
			C	H	O	X	C	H	O	X
MeSn[Co(CO) ₄] ₃	69-71	Red	24.2	0.5	29.7	-	23.4	0.4	27.0	-
BuSn[Co(CO) ₄] ₃	60-62	Red	28.0	1.3	27.9	-	29.0	1.4	27.4	-
VnSn[Co(CO) ₄] ₃ ^c	57-60	Red	25.5	0.5	29.2	0.0	25.9	0.5	30.1	0.0
PhSn[Co(CO) ₄] ₃ ^f	89-91	Red	30.5	0.7	27.1	-	29.6	0.5	30.1	-
Sn[Co(CO) ₄] ₄ ^g	Dec 140	V. dark red	24.0	0.0	31.9	-	24.5	0.0	32.7	-

^a Co: Calculated, 11.3; Found, 10.8.^b P: Calculated, 4.7; Found, 3.4.^c Vn = CH₂:CH-^d Co: Calculated, 26.5; Found, 28.7.^e Co: Calculated, 24.8; Found, 27.6^f Co: Calculated, 24.9; Found, 26.0.^g Sn: Calculated, 14.8; Found, 14.6. Co: Calculated, 29.3; Found, 27.7.

and X = Cl, Br and I.

The synthesis of these compounds is discussed in detail in the following sections, while spectroscopic studies are dealt with in Chapter V.

(i) Mono(tetracarbonylcobalt) Derivatives - Triphenyl(tetracarbonylcobalt)tin (IV) ($\text{Ph}_3\text{SnCo}(\text{CO})_4$) was prepared in methanol solution by reaction of $\text{Co}(\text{CO})_4^-$ on Ph_3SnCl , whereas all other derivatives were synthesised by allowing $\text{Co}_2(\text{CO})_8$ to react with an organotin halide or a tin tetrahalide:



$$n = 0, \text{X} = \text{Cl}, \text{Br}, \text{I}$$

$$n = 1, \text{R} = \text{Ph}, \text{X} = \text{Cl}, \text{Br}$$

$$n = 2, \text{R} = \text{Ph}, \text{X} = \text{Cl}, \text{Br}$$

$$\text{R} = \text{Me}, \text{X} = \text{Cl}.$$

The reaction was carried out by adding a solution of $\text{Co}_2(\text{CO})_8$ dropwise to a vigorously stirred solution of the tin halide at room temperature. The reactants were mixed slowly in order to avoid excess $\text{Co}_2(\text{CO})_8$, otherwise disubstitution tended to occur rendering purification of the final product difficult. The preparation of the trihalo derivatives was especially difficult from this point of view. The above reaction, when carried out with SnCl_4 in THF, afforded mainly $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$ even with slow mixing of the reagents. The only way to prepare the trihalo derivatives was to use benzene as solvent and have

excess SnX_4 present. The use of benzene also had the advantage that CoX_2 was precipitated and could be easily removed. The other derivatives $(\text{RX}_2\text{SnCo}(\text{CO})_4$ and $\text{R}_2\text{XSnCo}(\text{CO})_4$), however, could be made in THF solution using stoichiometric amounts of reactants as calculated from the above equation. The reaction mixtures were worked up in the usual way by evaporation of solvent, followed by pentane extraction. These derivatives could not be prepared by anion displacement reactions as di- and trisubstitution invariably occurred. Thus treatment of PhSnCl_3 with a methanol solution of $\text{Co}(\text{CO})_4^-$ afforded $\text{PhClSn}[\text{Co}(\text{CO})_4]_2$ only, while equimolar quantities of SnCl_4 and $\text{Co}(\text{CO})_4^-$ in THF gave $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$ and some $\text{ClSn}[\text{Co}(\text{CO})_4]_3$.

The iodo derivatives $\text{PhI}_2\text{SnCo}(\text{CO})_4$ and $\text{Ph}_2\text{ISnCo}(\text{CO})_4$ were prepared from the corresponding chloro derivatives by treatment with NaI in acetone solution.

The compounds prepared varied from white to red crystalline materials, and were all slightly air sensitive although several weeks exposure to air were needed for appreciable oxidation to occur.

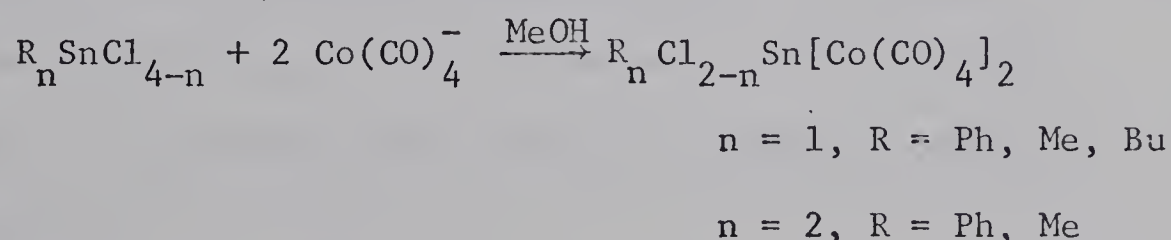
Triphenylphosphine Derivatives - Substitution of one CO by PPh_3

could be carried out by reaction of triphenylphosphine with $\text{R}_n\text{X}_{3-n}\text{SnCo}(\text{CO})_4$ to give $\text{R}_n\text{X}_{3-n}\text{SnCo}(\text{CO})_3\text{PPh}_3$. The ease with which this substitution occurred was influenced to a very large extent by n ; thus $\text{Br}_3\text{SnCo}(\text{CO})_4$ reacted rapidly with PPh_3

in benzene solution at room temperature with evolution of heat and formation of $\text{Br}_3\text{SnCo(CO)}_3\text{PPh}_3$, whereas $\text{PhCl}_2\text{SnCo(CO)}_4$ would only react with PPh_3 when the two were melted together at $80-100^\circ$, affording $\text{PhCl}_2\text{SnCo(CO)}_3\text{PPh}_3$, and $\text{BuCl}_2\text{SnCo(CO)}_4$ had to be heated to an even higher temperature (125°) to produce $\text{BuCl}_2\text{SnCo(CO)}_4$. Under similar reaction conditions, $\text{Ph}_2\text{ClSnCo(CO)}_4$ and $\text{Ph}_3\text{SnCo(CO)}_4$ would not react at all. This order of decreasing rate of substitution is the same as the order of decreasing carbonyl stretching frequencies, and therefore of increasing $\text{Co-C}\pi$ bonding (as discussed in detail in Chapter V). This is a reasonable relationship when one considers that a Co-C bond must be broken at some stage of the substitution and the rate will therefore depend upon the strength, and thus the bond order, of this bond. It is therefore possible to describe this decrease in rate of substitution in terms of increasing $\text{Co-C}\pi$ bonding irrespective of the exact mechanism. It is interesting to note that kinetic measurements carried out by Heck (99) on the reactions of phosphines with various acylcobalt carbonyls (RCOCo(CO)_4) showed the opposite trend, increasing the electron withdrawing ability of R decreased the rate of substitution. His measurements also showed that the rate of substitution was first order with respect to the acylcobalt tetracarbonyl, and independent of the concentration or nature of the phosphine.

This was taken as evidence for a dissociative mechanism, dissociation of RCOCo(CO)_4 into RCOCo(CO)_3 and CO being the rate determining step. He suggested that "electron withdrawing groups probably make dissociation more difficult because they remove electrons from the metal and make the loss of two more electrons with the departing ligand more unfavorable". This however assumed that Co-C π bonding is not altered by changing the electron withdrawing property of R. The reason for the difference between the trend reported in the present work and that reported by Heck remains, at present, obscure.

(ii) Bis(tetracarbonylcobalt) Derivatives - The majority of these compounds was prepared by treating organotin di- or trihalides with Co(CO)_4^- in methanol solution:



This was a very convenient method for preparation of these compounds as they could be crystallized in a reasonably pure state from the reaction mixture by cooling the methanol solution, filtering, and slowly adding water.

The dichloro compound ($\text{Cl}_2\text{Sn[Co(CO)}_4\text{]}_2$) was prepared by reaction of SnCl_4 in THF with NaCo(CO)_4 . $(\text{CH}_2\text{CH})\text{ClSn[Co(CO)}_4\text{]}_2$, together with $\text{CH}_2\text{CHSn[Co(CO)}_4\text{]}_3$, was made by treatment of one mole

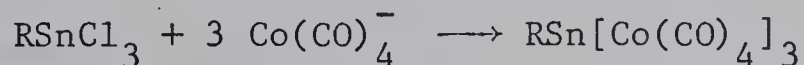
of $\text{CH}_2\text{CHSnCl}_3$ with 3 moles of NaCo(CO)_4 in THF.

The series $\text{X}_2\text{Sn[Co(CO)}_4\text{]}_2$ where $\text{X} = \text{Cl, Br, I and CH}_3\text{CO}_2$ were prepared by insertion reactions and will be discussed in more detail in Chapter IV.

The compounds prepared were yellow to red crystalline substances, and were somewhat more air sensitive than the mono derivatives described above, although they could still be safely handled in air for short periods. It was noted that the air sensitivity increased in the order

$\text{X}_2\text{Sn[Co(CO)}_4\text{]}_2 < \text{Ph}_2\text{Sn[Co(CO)}_4\text{]}_2 < \text{Me}_2\text{Sn[Co(CO)}_4\text{]}_2$. The latter compound was oxidised by only 15-30 minutes exposure to air, whereas $\text{Cl}_2\text{Sn[Co(CO)}_4\text{]}_2$ remained in air for several days without appreciable oxidation.

(iii) Tris(tetracarbonylcobalt) Derivatives - The organo derivatives $\text{RSn[Co(CO)}_4\text{]}_3$ were prepared by treating one mole of an organotin trihalide with 3 moles of Co(CO)_4^- in methanol or THF solution:



Use of methanol allowed the products to be crystallized out from the reaction mixture by cooling and adding water. The corresponding halo derivatives were made by treating SnX_4 with $\text{Co}_2(\text{CO})_8$ in THF solution in amounts given by the following equation:

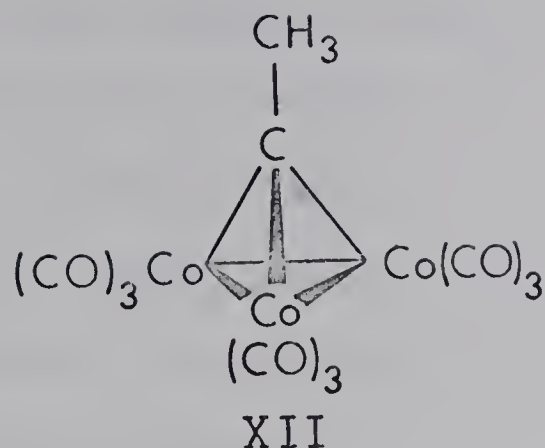


The reaction was usually complete in about 15 minutes as indicated by cessation of CO evolution. The product was isolated by the usual procedure, i.e. evaporation of THF in vacuo and extraction with n-pentane.

Both $\text{FSn}[\text{Co}(\text{CO})_4]_3$ and $\text{CH}_3\text{CO}_2\text{Sn}[\text{Co}(\text{CO})_4]_3$ were prepared by reaction of SnF_2 or $\text{Sn}[\text{CH}_3\text{CO}_2]_2$ with $\text{Co}_2(\text{CO})_8$. These reactions are believed to occur via an initial insertion reaction as discussed in detail in Chapter IV.

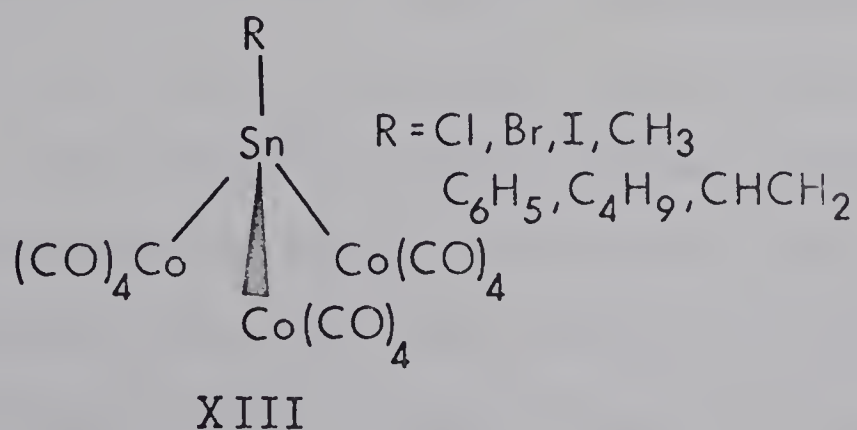
The organotin derivatives formed red, moderately air sensitive crystals, whereas the halo compounds ($\text{XSn}[\text{Co}(\text{CO})_4]_3$) crystallized as dark red needles and were less susceptible to atmospheric oxidation. All showed moderate thermal stability up to about 100° with the exception of $\text{ISn}[\text{Co}(\text{CO})_4]_3$ which decomposed on heating in cyclohexane producing $\text{Co}_4(\text{CO})_{12}$ identified by its infrared. This compound also decomposed in the mass spectrometer giving rise to fragments due to both $\text{ISn}[\text{Co}(\text{CO})_4]_3$ and $\text{Co}_4(\text{CO})_{12}$.

Trihalomethyl compounds X_3CY ($\text{Y} = \text{CH}_3, \text{Cl}, \text{F}, \text{C}_6\text{H}_5, \text{COOH}$, etc.) are reported (100,101) to react with $\text{Co}_2(\text{CO})_8$ with formation of tris(tricarbonylcobalt) derivatives $\text{YCo}_3(\text{CO})_9$ which have structures such as XII, as shown by an X-ray determination (102) and which possess Co-Co bonds.



A similar derivative of silicon ($\text{CH}_2\text{CHSiCo}_3(\text{CO})_9$) was reported in the reaction of tetravinylsilane with cobalt carbonyl (103). However more recent work has cast some doubt upon the nature of the product of this reaction. Attempts to repeat the reaction afforded $\text{ClCCo}_3(\text{CO})_9$ (104).

In contrast to this, RSnCl_3 and SnX_4 reacted with $\text{Co}(\text{CO})_4^-$ and $\text{Co}_2(\text{CO})_8$ respectively affording the tris(tetracarbonylcobalt) derivatives $\text{RSn}[\text{Co}(\text{CO})_4]_3$ (XIII) as described above, rather than the tricarbonylcobalt compounds $\text{RSnCo}_3(\text{CO})_9$.

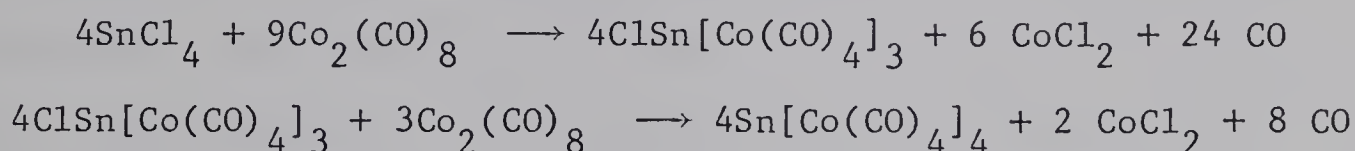


This was shown conclusively by elemental analysis and mass spectra in which peaks assigned to $\text{RSnCo}_3(\text{CO})_{11}^+$, and in two cases to $\text{RSnCo}_3(\text{CO})_{12}^+$, appeared. The mass spectra are discussed in more detail in Chapter V. It was previously reported (105) that BuSnCl_3 reacted with $\text{Co}_2(\text{CO})_8$ to give $\text{BuSnCo}_3(\text{CO})_9$. However, on repeating the reaction only $\text{BuSn}[\text{Co}(\text{CO})_4]_3$ could be isolated.

Attempts to convert $\text{RSn}[\text{Co}(\text{CO})_4]_3$ into $\text{RSnCo}_3(\text{CO})_9$ by heat and ultraviolet irradiation all met with failure. Heating $\text{MeSn}[\text{Co}(\text{CO})_4]_3$ in a sealed tube to 90° for one hour had no effect, unreacted starting material being recovered, whereas refluxing in toluene for 5 hours caused complete decomposition. After ultra-violet irradiation of a hexane solution of this compound, the infrared spectrum showed only starting material, $\text{Co}_4(\text{CO})_{12}$ and $\text{Co}_2(\text{CO})_8$ to be present.

The reason for the ease with which $\text{RCoCo}_3(\text{CO})_9$ derivatives can be prepared, while tin forms only tetracarbonylcobalt derivatives may in part be the larger size of the tin atom compared to that of carbon. This may prevent the cobalt atoms approaching close enough to form cobalt-cobalt bonds with elimination of CO. The X-ray structure of $\text{BrSn}[\text{Co}(\text{CO})_4]_3$ is being determined by Mr. R. Ball of this University.

(iv) Tetrakis(tetracarbonylcobalt)tin(IV) - The final member of the $R_n Sn[Co(CO)_4]_{4-n}$ series ($Sn[Co(CO)_4]_4$), was prepared by the reaction of either $ClSn[Co(CO)_4]_3$, or $SnCl_4$, with excess $Co_2(CO)_8$ in THF solution:



The reaction was slow, taking about 24 hours for completion. The product crystallized out from the THF solution during the course of the reaction as small very dark red glistening crystals. It is only slightly soluble in n-pentane and hexane (in the order of lg./l), and is not much more soluble in acetone and THF. It is however sufficiently soluble to be crystallized by evaporation of saturated pentane or acetone solutions to small volume. It is not possible to obtain absolutely pure material by these methods, as the compound tends to lose CO fairly easily, especially in vacuo, in fact heating to 70° in vacuo causes complete decomposition with the production of an apparently crystalline and magnetic powder which is presumably a tin/cobalt alloy. Indeed, whenever recrystallized $Sn[Co(CO)_4]_4$ is redissolved, there is always a small quantity of black insoluble material left.

The constitution of this compound was confirmed by elemental analysis, a molecular weight determination which gave a value of 880 ± 100 compared to a theoretical value of

802.7, and its mass spectrum in which fragments up to $\text{SnCo}_4(\text{CO})_{15}^+$ were observed.

This compound represents one of only a few known examples in which four transition metals are bonded to a main group metal. Such compounds include $\text{SnFe}_4(\text{CO})_{16}$ (which however also has Fe-Fe bonds) (106), $\text{Sn}[\text{Fe}(\text{CO})_2\text{Cp}]_4$ (82), and $[\text{Cp}(\text{CO})_2\text{Fe}]_2\text{Sn}[\text{Mo}(\text{CO})_3\text{Cp}]_2$ (84). After completion of the present work the preparation of $\text{Sn}[\text{Co}(\text{CO})_4]_4$ was reported by Bigorgne and Quintin (107) using a procedure essentially the same as that described in the present work. It involved reaction of SnCl_2 with an excess of $\text{Co}_2(\text{CO})_8$, and presumably proceeded via initial formation of the insertion product $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$, and subsequent reaction of this with $\text{Co}_2(\text{CO})_8$.

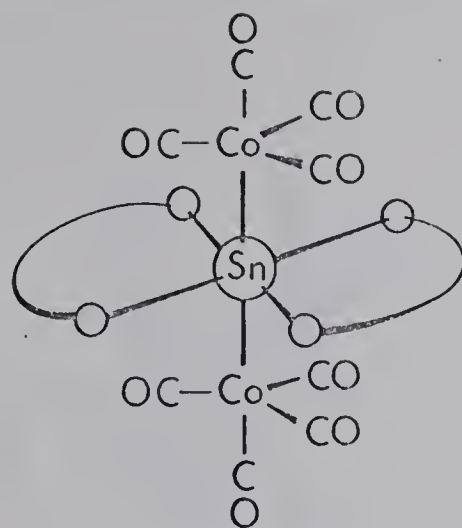
(v) Reaction of bis(acetylacetonate)tin dichloride with $\text{Co}(\text{CO})_4^-$ -

Attempts to prepare $(\text{acac})_2\text{Sn}[\text{Co}(\text{CO})_4]_2$ by treatment of $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$ with thallium (I) acetylacetonate ($\text{Tl}(\text{acac})$) were unsuccessful, only $\text{ClSn}[\text{Co}(\text{CO})_4]_3$ could be isolated. Possibly the acetylacetonate anion displaces both Cl^- and $\text{Co}(\text{CO})_4^-$, and the latter reacts with more $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$ to give the observed product.

Attempts were then made to prepare the acetylacetonate derivative by treating $(\text{acac})_2\text{SnCl}_2$ with $\text{Co}(\text{CO})_4^-$. The reaction was found to be more complex than anticipated, different products being obtained under different conditions. When a THF solution of $\text{NaCo}(\text{CO})_4$ was added very slowly to $(\text{acac})_2\text{SnCl}_2$

in the same solvent, and the reaction mixture worked up in the usual manner, i.e. evaporation of solvent and extraction with n-pentane, an orange crystalline material was obtained which was shown to be $(\text{acac})_2\text{Sn}[\text{Co}(\text{CO})_4]_2$ by elemental analysis. Its infrared spectrum showed bands due to terminal carbonyl groups (Figure 30, Chapter V) and bands due to chelated acetylacetonate groups. Its molecular weight in cyclohexane was found to be dependent upon the concentration, at 1.07 mg./ml. it was 670 ± 51 , whereas at 27.2 mg./ml. it was 741 ± 4 compared to the calculated value of 658.9.

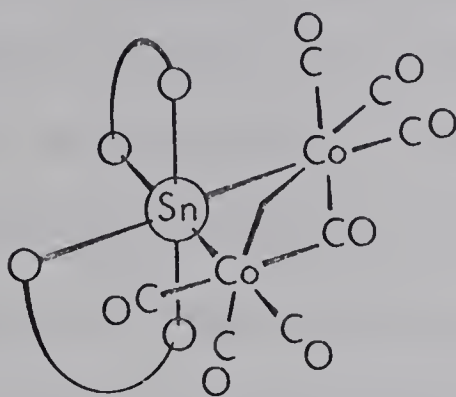
Association has been observed in other acetylacetonate complexes (108) and may result in this case from a change of chelating to bridging acac groups. The highest mass fragment observed in the mass spectrum corresponded to $(\text{acac})_2\text{SnCo}_2(\text{CO})_7^+$ which was considered to be one CO group less than the molecular ion. The absence of parent ion was frequently observed for tetracarbonylcobalt derivatives, and is discussed in detail in Chapter V. On the basis of the above evidence, and the observations discussed below, this compound is believed to be trans- $(\text{acac})_2\text{Sn}[\text{Co}(\text{CO})_4]_2$ (XIV).



XIV

If the solution of NaCo(CO)_4 was added very rapidly to $(\text{acac})_2\text{SnCl}_2$, and the reaction mixture worked up in the same way as above, the product was a red crystalline material which analysed as $(\text{acac})_2\text{SnCo}_2(\text{CO})_7$. This was supported by the appearance in the mass spectrum of a fragment at $m/e = 632$ which was the highest mass fragment observed, and was shown to correspond to $(\text{acac})_2\text{SnCo}_2(\text{CO})_7^+$ by an exact mass determination. Neither of these methods absolutely excludes the possibility that the compound is an octacarbonyl; analytical differences are slight, and other tin derivatives of cobalt carbonyl are known in which the fragment of highest m/e is one CO group less than the molecular ion. However, the infrared spectrum (Figure 40, Chapter V) possesses 5 bands in the terminal carbonyl region

and one at 1836 cm^{-1} which is assigned to a bridging carbonyl group. On this evidence structure XV is suggested.



XV

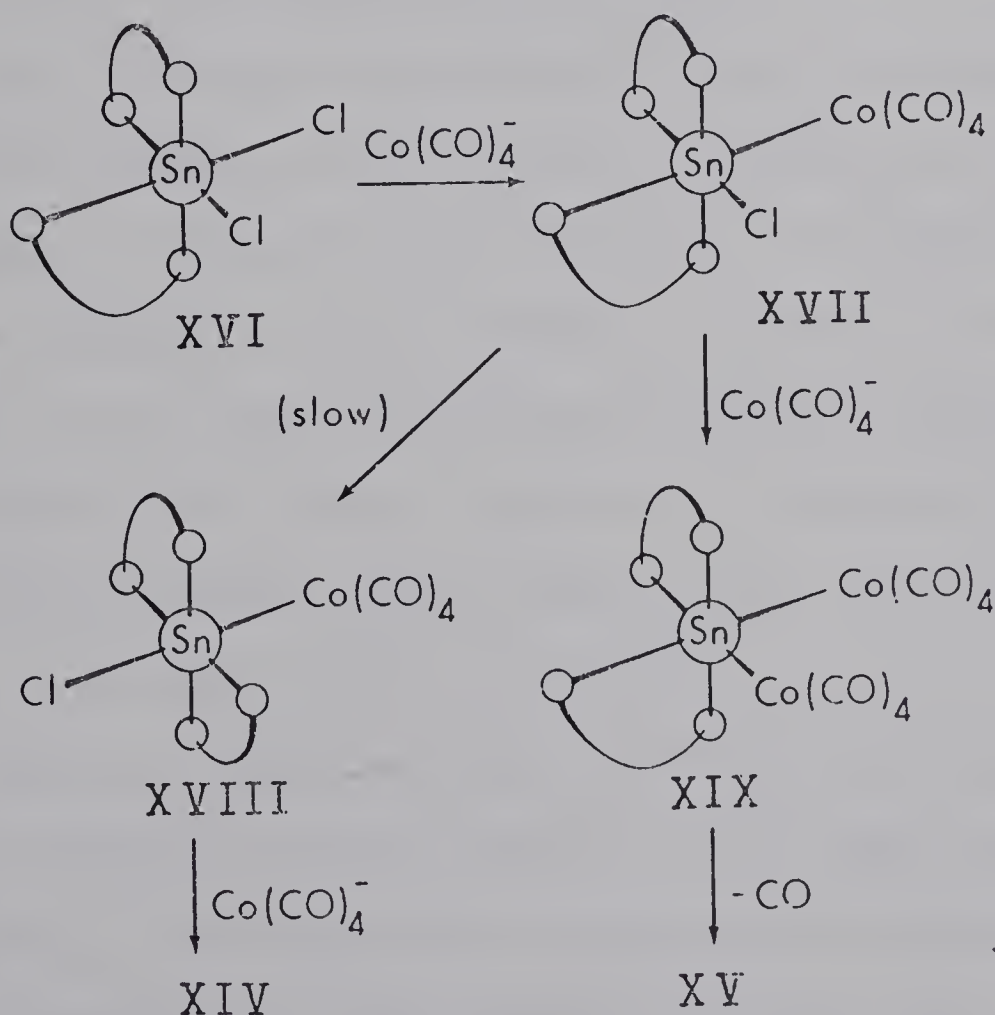
The structure proposed preserves an approximately octahedral configuration around both tin and cobalt. The cobalt-cobalt bond, pictured as bent, is postulated to preserve the inert gas configuration for both cobalt atoms. Structure XV can be regarded as derived from the dicobalt octacarbonyl structure by replacing one of the bridging carbonyl groups with the $(\text{acac})_2\text{Sn}$ moiety. From this viewpoint, it is related to the structure of $\text{HC}=\text{CHC}(\text{O})\text{OCCo}_2(\text{CO})_7$, in which two cobalt atoms are bridged by a carbon atom of a lactone ring (109).

The nmr spectrum of XV, while not inconsistent with the proposed structure, does not establish it unambiguously. In benzene solution only two signals were observed at τ 5.62 and

and 8.99 in an intensity ratio of 1:5.8 due to the CH and CH₃ protons of the acetylacetonate ligands. However, for a cis configuration of acac rings, as in XV, there are two pairs of nonequivalent methyl groups, and a splitting of the methyl signal might be expected, as is observed with (acac)₂SnCl₂ (110). No indication of splitting was observed, however. Since the splitting was not expected to be large (it was only 0.02 ppm for benzene solutions of (acac)₂SnCl₂), it may have been obscured by broadening of the signal caused by the quadrupole moment of the cobalt atoms. Also, it has been reported that splitting in the cis-dihalides is not observed at higher temperatures (111), and it was suggested that this was due to a rapid interconversion of the two enantiomers of the cis configuration. This interconversion could occur either via a "twist" mechanism involving a C_{2v} intermediate, or via a five-coordinate intermediate in which a chelating acac group becomes monodentate. It is possible that a similar interconversion is in operation at room temperature in the present case.

The decisive influence of the rate of addition on the products can be plausibly accounted for. Previous work (110, 111) has indicated that (acac)₂SnCl₂ has a cis configuration as shown in XVI. Displacement of chloride ion by an initial Co(CO)₄⁻ anion would produce the intermediate cis-(acac)₂Sn(Cl)Co(CO)₄, XVII. It is postulated that XVII

isomerizes to the trans configuration XVIII relatively slowly. Rapid addition of a second mole of Co(CO)_4^- would result in displacement of chloride from XVII before isomerization could occur. This would produce the cis-bis(tetracarbonylcobalt) intermediate XIX which is assumed to eliminate carbon monoxide in an intramolecular condensation, yielding XV, in which the CO bridged Co-Co bond holds the molecule in a cis configuration. However, if Co(CO)_4^- is added slowly, XVII is permitted to isomerize to XVIII before the second chloride ion is displaced, and XIV is the product. The postulated structures XIV and XV are thus consistent with the above reaction scheme.



Facile condensation of the intermediate XIX seems reasonable because the Co-Sn-Co bond angle is probably close to 90° thus bringing the two $\text{Co}(\text{CO})_4$ groups sufficiently close to interact. Bis(tetracarbonylcobalt)derivatives of four-coordinate tin, on the other hand, do not spontaneously undergo such a condensation, presumably because the larger Co-Sn-Co bond angle (probably in the order of 110 to 120°) prevents a sufficiently close approach at the $\text{Co}(\text{CO})_4$ groups. That the Co-Sn-Co angle is greater than the tetrahedral angle of 109° is reasonable, as X-ray studies of related derivatives of tin have shown values ranging from 117° (in $\text{Ph}_2\text{Sn}[\text{Mn}(\text{CO})_5]_2$ (60)), to 128.6° (in $\text{Cl}_2\text{Sn}[\text{Fe}(\text{CO})_2\text{Cp}]_2$ (112)).

While the above reaction scheme accounts qualitatively for the main features of the reaction of $\text{NaCo}(\text{CO})_4^-$ with $(\text{acac})_2\text{SnCl}_2$, it should be noted that other more complex processes undoubtedly occurs. Yields of the desired products were low, of the order of 10-15% and considerable material was formed which was not soluble in n-pentane. Furthermore, $\text{ClSn}[\text{Co}(\text{CO})_4]_3$ was also isolated implying that one process involved displacement of the acac ligands.

The mono(tetracarbonylcobalt) derivative $(\text{acac})_2\text{Sn}(\text{Cl})\text{Co}(\text{CO})_4$ was also isolated in very low yield by using a large excess of $(\text{acac})_2\text{SnCl}_2$. This compound was characterized by analysis and infrared spectrum; the latter showed four bands in the terminal carbonyl stretching region, with positions and intensity

distribution very similar to those of other mono(tetracarbonyl-cobalt) derivatives of C_s symmetry.

(vi) Reaction of Tetravinyltin with Dicobalt Octacarbonyl - It

was reported that tetravinylsilane reacted with $Co_2(CO)_8$ with the formation of $CH_2CHSiCo_3(CO)_9$ (103). In an attempt to extend this to tin, a solution of tetravinyltin in THF was treated with $Co_2(CO)_8$ in the same solvent. After allowing it to react for 15 minutes at room temperature, THF was removed under reduced pressure. During the latter process much gas was evolved. By pentane extraction of the residue only $Co_4(CO)_{12}$ and $CH_3CCo_3(CO)_9$ were isolated. However when the reaction was carried out in refluxing n-pentane a liquid formulated as $(CH_2CH)_2Sn[Co(CO)_4]_2$ was isolated, and was characterized by comparison of the infrared spectrum with other $R_2Sn[Co(CO)_4]_2$ derivatives.

EXPERIMENTAL

Melting points were determined by use of a Gallenkamp melting-point apparatus with the sample sealed in an evacuated melting-point tube to prevent atmospheric oxidation. All values are uncorrected. Microanalyses were performed by Bernhardt Mikroanalytisches Laboratorium (Mülheim), by Pascher Mikroanalytisches Laboratorium (Bonn) and by Mrs. Darlene Mahlow of the University of Alberta Chemistry Department Microanalytical Laboratory.

Molecular weights were measured with a Mechrolab Osmometer in cyclohexane solution under an Argon atmosphere. Argon saturated with cyclohexane vapour was introduced into the chamber of the Osmometer at a rate of about 9 cm^3 per minute, the chamber being maintained at 37° .

All reactions and subsequent operations were carried out under a static nitrogen atmosphere maintained at a slight positive pressure by a bubbler. All products were handled with minimum exposure to air.

Solvents and Starting Materials

Tetrahydrofuran (THF): Fischer certified THF was freed from moisture and traces of peroxide by distillation from lithium aluminum hydride and used freshly distilled.

In every other case reagent grade solvents were employed without further purification.

Sodium Amalgam: Mercury (100 g.) was placed in a one-neck 250 ml. flask fitted with a side-arm and stopcock. The flask was tilted so that the side-arm was above the level of the mercury. The mercury was stirred with a magnetic stirrer and nitrogen blown over it via the side-arm. Sodium metal (1.0 g.) was cut into thin slices under n-pentane and cautiously added to the mercury, after holding in the nitrogen stream to remove excess pentane.

When all the sodium had been added, the amalgam was cooled to room temperature, and the reduction of cobalt carbonyl carried out in the same apparatus.

Dicobalt Octacarbonyl: This was prepared by the method described by Jolly (113). Cobalt carbonate (250 g.) was suspended in 900 ml. of hexane, contained in a glass liner which was placed inside a two litre Magne stirrer autoclave. It was then filled to 1850 lbs./in.² with CO, and then to 3700 lbs./in.² with H₂, and heated 150-160° for four hours with continuous stirring. After allowing it to cool to room temperature, the autoclave was opened and the glass liner removed. The solution of Co₂(CO)₈ was quickly filtered, placed in a stoppered flask, and cooled overnight in the freezing compartment of a refrigerator. Pure Co₂(CO)₈ crystallized out, a typical yield being 140 g. The cobalt carbonyl produced in this way was not further purified. It was stored in the freezer in nitrogen-filled containers to prevent further oxidation.

Methylgermanium triiodide: This was prepared by the procedure described by Brauer (114). Germanium diiodide (5.0g.) and 2.4g. of methyl iodide were placed in a thick walled tube which was cooled to -80° , evacuated and sealed. The tube was then heated to 110° for 24 hours. After opening the tube, the contents were extracted with n-pentane. The extract was filtered, evaporated to a small volume, and cooled to -20° . A yield of 4.0g. of product was obtained and was purified by n-pentane crystallization.

Phenylgermanium trichloride: This was prepared by the procedure of Rykens and Van der Kerk (115). A mixture of tetraphenylgermane (10.0g., 26.3mmole.), germanium tetrachloride (13.75g., 64.1mmole.) and aluminum trichloride (0.7g., 5.3mmole.) were sealed into an evacuated Carius tube and heated to 110° - 120° for 12 hours. The contents of the tube were distilled in vacuo, the product distilling over at 100 - 102° (14mm). Yield 12.0g.

Bis(acetylacetonato)tin dichloride: This was prepared by the method of Morgan and Drew (116). Stannic chloride (6.8g., 26.1mmole.) was dissolved in 50 ml. of dry chloroform contained in a round-bottomed flask which was fitted with a reflux condenser. Acetylacetone (2.7g., 27.0mmole.) was added with vigorous stirring, heat was evolved, and a white precipitate formed. A further 2.7g. portion of acetylacetone was then slowly added, and the mixture refluxed for 3 hours in a fume

hood (because of HCl evolution). At the end of this period the precipitate had dissolved leaving a clear slightly brown solution. The solvent was then removed under reduced pressure, and the buttery residue dissolved in benzene. This solution was then evaporated to about 10 ml. and n-pentane slowly added. The initial oily brown material which was precipitated was rejected, and the white crystalline material which came down on further n-pentane addition was kept and recrystallized from the same solvent system. The product was dried in vacuo. The yield was 9.0g.

Preparation of Tetracarbonylcobalt Derivatives

The majority of these were prepared by one of the following general methods. Table V lists the quantities of reactants, solvents and conditions used, together with the method employed and the yields obtained.

A. Halide Displacement by NaCo(CO)_4 in THF Solution: A THF solution of NaCo(CO)_4 was prepared by sodium amalgam reduction of $\text{Co}_2(\text{CO})_8$. In a typical reaction 1.71g. (5.0mmole) of $\text{Co}_2(\text{CO})_8$ was dissolved in about 50 ml. of freshly distilled THF and placed in the flask used to prepare the sodium amalgam as described above, and which contained about 50g. of sodium amalgam. The mixture was stirred rapidly at room temperature. The reaction was complete when the originally dark red solution became yellow or grey. This took about 30 minutes. This solution should now contain 10.0mmole. of NaCo(CO)_4 .

TABLE V

Experimental Data for the Preparation of Tetracarbonylcobalt Derivatives of Germanium and Tin

Compound	Halide	Mmole.	Carbonyl	Mmole.	Method ^a	Reaction Solvent	Recryst. Solvent	%age. Yield
$\text{Cl}_3\text{GeCo}(\text{CO})_4$	GeCl_4	10.0	$\text{NaCo}(\text{CO})_4$	11.0	A	THF	pent. ^b	57
$\text{Cl}_3\text{GeCo}(\text{CO})_4$	GeCl_4	23.3	$\text{Co}_2(\text{CO})_8$	18.9	C2	THF	pent.	49
$\text{Br}_3\text{GeCo}(\text{CO})_4$	GeBr_4	5.1	$\text{Co}_2(\text{CO})_8$	3.8	C2	THF	pent.	20
$\text{I}_3\text{GeCo}(\text{CO})_4$	GeI_4	5.0	$\text{Co}_2(\text{CO})_8$	3.8	C2	THF	pent.	50
$\text{Cl}_2\text{PhGeCo}(\text{CO})_4$	PhGeCl_3	4.7	$\text{NaCo}(\text{CO})_4$	15.9	A	THF	pent.	40
$\text{I}_2\text{MeGeCo}(\text{CO})_4$	MeGeI_3	3.6	$\text{NaCo}(\text{CO})_4$	4.0	A	THF	pent.	65
$\text{ClPh}_2\text{GeCo}(\text{CO})_4$	Ph_2GeCl_2	10.0	$\text{NaCo}(\text{CO})_4$	23.2	A	THF	pent.	37
$\text{ClMe}_2\text{GeCo}(\text{CO})_4$	Me_2GeCl_2	4.6	$\text{NaCo}(\text{CO})_4$	7.0	A	THF	pent.	30
$\text{Ph}_3\text{GeCo}(\text{CO})_4$	Ph_3GeBr	9.5	$\text{Co}(\text{CO})_4^-$	9.1	B	MeOH	pent.	30
$\text{Cl}_2\text{Ge}[\text{Co}(\text{CO})_4]_2$	GeCl_4	2.3	$\text{Co}_2(\text{CO})_8$	5.9	C2	THF	pent.	70
$\text{IMeGe}[\text{Co}(\text{CO})_4]_2$	MeGeI_3	4.7	$\text{NaCo}(\text{CO})_4$	17.6	A	THF	pent.	70
$\text{Me}_2\text{Ge}[\text{Co}(\text{CO})_4]_2$	Me_2GeCl_2	10.0	$\text{NaCo}(\text{CO})_4$	21.0	A	THF	pent.	30
$\text{Cl}_3\text{SnCo}(\text{CO})_4$	SnCl_4	96.0	$\text{Co}_2(\text{CO})_8$	29.0	C1	C_6H_6	pent.	15

TABLE V (continued)

Compound	Halide	Mmole.	Carbonyl	Mmole.	Method ^a	Reaction Solvent	Recryst. Solvent	%age. Yield
$\text{Br}_3\text{SnCo}(\text{CO})_4$	SnBr_4	29.7	$\text{Co}_2(\text{CO})_8$	16.4	Cl	C_6H_6	pent.	85
$\text{I}_3\text{SnCo}(\text{CO})_4$	SnI_4	4.8	$\text{Co}_2(\text{CO})_8$	3.8	Cl	C_6H_6	pent.	65
$\text{Cl}_2\text{PhSnCo}(\text{CO})_4$	PhSnCl_3	11.6	$\text{Co}_2(\text{CO})_8$	5.8	Cl	THF	pent.	30
$\text{Cl}_2\text{BuSnCo}(\text{CO})_4$	BuSnCl_3	19.8	$\text{Co}_2(\text{CO})_8$	14.6	Cl	THF	pent.	60
$\text{Br}_2\text{PhSnCo}(\text{CO})_4$	PhSnBr_3	9.2	$\text{Co}_2(\text{CO})_8$	5.8	Cl	THF	pent.	60
$\text{ClPh}_2\text{SnCo}(\text{CO})_4$	Ph_2SnCl_2	9.9	$\text{Co}_2(\text{CO})_8$	7.3	Cl	THF	pent.	70
$\text{ClMe}_2\text{SnCo}(\text{CO})_4$	Me_2SnCl_2	20.5	$\text{Co}_2(\text{CO})_8$	16.6	Cl	THF	pent.	55
$\text{BrPh}_2\text{SnCo}(\text{CO})_4$	Ph_2SnBr_2	3.9	$\text{Co}_2(\text{CO})_8$	2.9	Cl	THF	pent.	50
$\text{Ph}_3\text{SnCo}(\text{CO})_4$	Ph_3SnCl	5.0	$\text{Co}(\text{CO})_4^-$	5.0	B	MeOH	$\text{MeOH}/\text{H}_2\text{O}$	50
$\text{Me}_3\text{SnCo}(\text{CO})_4^c$	Me_3SnCl	4.0	$\text{Co}(\text{CO})_4^-$	4.0	B	MeOH	sublimed	35
$\text{Ph}_3\text{PbCo}(\text{CO})_4$	Ph_3PbCl	4.9	$\text{Co}(\text{CO})_4^-$	6.0	B	MeOH	pent.	65
$\text{ClPhSn}[\text{Co}(\text{CO})_4]_2$	PhSnCl_3	2.5	$\text{Co}(\text{CO})_4^-$	5.0	B	MeOH	$\text{MeOH}/\text{H}_2\text{O}$	70
$\text{ClMeSn}[\text{Co}(\text{CO})_4]_2$	MeSnCl_3	4.0	$\text{Co}(\text{CO})_4^-$	8.0	B	MeOH	$\text{MeOH}/\text{H}_2\text{O}$	60
$\text{ClBuSn}[\text{Co}(\text{CO})_4]_2$	BuSnCl_3	10.0	$\text{Co}(\text{CO})_4^-$	10.0	B	MeOH	pent.	70

TABLE V (continued)

Compound	Halide	Mmole.	Carbonyl	Mmole.	Method ^a	Reaction Solvent	Recryst. Solvent	%age. Yield
$\text{ClVnSn}[\text{Co}(\text{CO})_4]_2^{\text{d}}$	VnSnCl_3	5.0	$\text{NaCo}(\text{CO})_4$	15.8	A	THF	pent.	15 ^e
$\text{Ph}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$	Ph_2SnCl_2	2.5	$\text{Co}(\text{CO})_4^-$	5.0	B	MeOH	$\text{MeOH}/\text{H}_2\text{O}$	55
$\text{Me}_2\text{Sn}[\text{Co}(\text{CO})_4]_2^{\text{c}}$	Me_2SnCl_2	1.7	$\text{Co}(\text{CO})_4^-$	3.4	B	MeOH	$\text{MeOH}/\text{H}_2\text{O}$	-
$\text{ClSn}[\text{Co}(\text{CO})_4]_3$	SnCl_4	40.0	$\text{Co}_2(\text{CO})_8$	90.6	C2	THF	pent.	75
$\text{BrSn}[\text{Co}(\text{CO})_4]_3$	SnBr_4	9.8	$\text{Co}_2(\text{CO})_8$	22.5	C2	THF	pent.	65
$\text{ISn}[\text{Co}(\text{CO})_4]_3$	SnI_4	4.9	$\text{Co}_2(\text{CO})_8$	9.1	C2	THF	pent.	75
$\text{PhSn}[\text{Co}(\text{CO})_4]_3$	PhSnCl_3	9.6	$\text{NaCo}(\text{CO})_4$	32.0	A	THF	pent.	70
$\text{MeSn}[\text{Co}(\text{CO})_4]_3$	MeSnCl_3	5.8	$\text{Co}(\text{CO})_4^-$	17.0	B	MeOH	pent.	50
$\text{BuSn}[\text{Co}(\text{CO})_4]_3$	BuSnCl_3	5.0	$\text{NaCo}(\text{CO})_4$	20.5	A	THF	pent.	60
$\text{VnSn}[\text{Co}(\text{CO})_4]_3$	VnSnCl_3	5.0	$\text{NaCo}(\text{CO})_4$	15.8	A	THF	pent.	20 ^e

^a A, B, C1 and C2 refer to the four methods described in the Experimental section of Chapter II.

^b pent. = n-pentane.

^c These compounds were first prepared by Mrs. H.R.H. Patil in this laboratory by different methods.

^d $\text{Vn} = \text{CH}_2:\text{CH}-$

^e Both $\text{ClVn}[\text{Co}(\text{CO})_4]_2$ and $\text{VnSn}[\text{Co}(\text{CO})_4]_3$ isolated.

However, some decomposition inevitably occurs, as evidenced by slight CO evolution, and a small percentage of $\text{Hg}[\text{Co}(\text{CO})_4]_2$ is also formed (97); consequently a small excess of $\text{Co}_2(\text{CO})_8$ was commonly employed. The flask was then tilted so that the stopcock and side-arm were under the mercury, and the excess amalgam was run off. The $\text{NaCo}(\text{CO})_4$ solution was then run into a flask containing the required amount of organo-metallic halide, or metal halide, dissolved in THF and stirred with a magnetic stirrer, the quantities used being given in Table V. For every mole of halide, one, two or three moles of $\text{NaCo}(\text{CO})_4$ were employed depending on whether a mono-, bis- or tris(tetracarbonylcobalt) derivative was desired. The THF solution was then stirred at room temperature for 5-15 minutes, after which time the THF was removed under a water pump vacuum on a rotary evaporator. When all the THF had been removed, the resulting solid or oily residue was shaken with 20-50 ml. portions of n-pentane until no more material was dissolved. The combined extracts were then filtered or centrifuged and evaporated on a rotary evaporator, either until crystals began to form, or until the volume was down to about 5 ml. The solution was then cooled to -20° to complete the crystallization. If no crystals came down, the solution was evaporated in a stream of nitrogen to a smaller volume and cooled in the freezer until crystals did form. The product was then invariably recrystallized

from n-pentane.

B. Halide Displacement by $\text{Co}(\text{CO})_4^-$ in Methanol Solution: The $\text{Co}(\text{CO})_4^-$ anion was prepared in methanol solution by dissolving $\text{Co}_2(\text{CO})_8$ in methanol and heating the solution to 50° . Typically, 1.0g. (3.0mmole.) of $\text{Co}_2(\text{CO})_8$ was dissolved in 25 ml. of methanol contained in a 50 ml. round-bottom flask in which an atmosphere of nitrogen was maintained. The solution was then heated to 50° in a water bath causing rapid CO evolution. Heating was continued until no more CO was evolved, and the solution had become pale red. The solution, which now contained 4.0mmole. of $\text{Co}(\text{CO})_4^-$, was centrifuged under nitrogen in stoppered centrifuge tubes. It was then added to a stirred solution of the required amount of the appropriate organometal halide dissolved in about 10 ml. of methanol. The proportions of $\text{Co}(\text{CO})_4^-$ to halide used are given in Table V. After stirring for 5-15 minutes, the solution was cooled in ice, and air-free distilled water added slowly to precipitate crystalline product. The product crystallized out in a reasonably pure state, but was usually recrystallized from n-pentane, or methanol/water, and then dried in vacuo at room temperature.

C. Reaction of Halide with Dicobalt Octacarbonyl: These reactions involve treatment of an organometal halide or metal tetrahalide with cobalt carbonyl in THF or benzene solution.

1. Preparation of Mono(tetracarbonylcobalt)tin (IV) Derivatives -

In the preparation of these compounds ($R_n X_{3-n} SnCo(CO)_4$, $n = 0, 1, 2$), the cobalt carbonyl solution was added very slowly to the appropriate tin halide ($R_n SnX_{4-n}$, $n = 0, 1, 2$) in order to prevent substitution of more than one halide ion. The preparation of the trihalotin compounds differed from the preparation of the other derivatives in the use of benzene, rather than THF, as a reaction solvent. The quantities of reactants employed are given in Table V.

In a typical preparation 10 mmole. of the tin halide was dissolved in 10-20 ml. of the appropriate solvent (benzene for SnX_4 , and THF for $R_n SnX_{3-n}$ and $R_2 SnX_2$), and the solution stirred at room temperature with a magnetic stirrer. A solution of the required amount of $Co_2(CO)_8$, at a concentration of about 10 mmole. per 100 ml. was then added dropwise from an addition funnel at such a rate that addition was complete in one to two hours. The solution was stirred for a further 30 minutes, after addition of cobalt carbonyl, to ensure completion of the reaction. Solvent was then removed from the reaction mixture by evaporation under reduced pressure on a rotary evaporator (benzene solutions being first filtered free of precipitated CoX_2). The residue from this operation was next extracted with small portions of n-pentane until no more material was dissolved. The extracts were combined, filtered and evaporated until

crystallization commenced, or the volume was reduced to 2-5 ml. The solution was then cooled to -20° to complete crystallization from n-pentane.

2. Preparation of Other Derivatives - The following method was used to prepare mono- and bis(tetracarbonylcobalt) derivatives of germanium, and tris(tetracarbonylcobalt) derivatives of tin.

A solution containing 5 mmole. of the appropriate halide in 50-100 ml. of THF was added to the required amount of $\text{Co}_2(\text{CO})_8$ (see Table V) in the same solvent which was stirred vigorously at room temperature. The halide solution was added cautiously at first because of initial rapid CO evolution. When halide addition was complete, the solution was stirred until CO evolution had ceased (15-30 minutes). The reaction mixture was then worked up as described in C1, i.e. evaporation of solvent and extraction with n-pentane.

In both C1 and C2 the reactions were carried out in a fume hood because of the large volumes of toxic carbon monoxide evolved.

Preparation of Iodo-derivatives - The derivatives $\text{PhI}_2\text{MCo}(\text{CO})_4$ and $\text{PhIMCo}(\text{CO})_4$, where M = Sn or Ge, were prepared from the corresponding chloro-derivative by treatment with NaI in acetone solution. Typically, 1.0 mmole. of $\text{Ph}_2\text{IMCo}(\text{CO})_4$ or 0.5 mmole. $\text{PhI}_2\text{MCo}(\text{CO})_4$ were dissolved in acetone, and 1.0 mmole. of NaI, dissolved in the same solvent, was added with stirring at room temperature. NaCl precipitated out, and

was removed by centrifuging. The acetone solution was evaporation at reduced pressure and the residue dissolved in n-pentane. After centrifuging, evaporation to incipient crystallization, and cooling to -20° , a yield of 50-60% of product was obtained, after recrystallization from n-pentane at -20° .

Tribromo(tricarbonyltriphenylphosphinecobalt)tin (IV),

$\text{Br}_3\text{SnCo(CO)}_3\text{PPh}_3$: A solution of 1.0 g. (1.9 mmole.) of $\text{Br}_3\text{SnCo(CO)}_4$ in the minimum amount of benzene was prepared and to this 0.6 g. (2.3 mmole.) of PPh_3 was slowly added with stirring at room temperature. Vigorous CO evolution occurred and the solution became warm. Solid material began to precipitate, and this was completed by addition of n-pentane. The solid was filtered off and redissolved in 50 ml. of benzene leaving an insoluble residue. The benzene was evaporated to 10 ml. and n-pentane slowly added. The initially formed greenish impure deposit was rejected, and the solution cooled to -20° after a total of 80 ml. of n-pentane had been added. This afforded 0.25 g. glistening orange crystals which were recrystallized from benzene and n-pentane.

Dichlorobutyl(tricarbonyltriphenylphosphinecobalt)tin(IV),

$\text{Cl}_2(\text{C}_4\text{H}_9)\text{SnCo(CO)}_3\text{PPh}_3$: A mixture of 1.0 g. (2.4 mmole.) of $\text{Cl}_2(\text{C}_4\text{H}_9)\text{SnCo(CO)}_4$ and 0.7 g. (2.7 mmole.) of PPh_3 was heated under N_2 to 125° in an oil bath. After cessation of CO evolution (about one hour), the mixture was cooled and extracted with a small amount of n-pentane to remove unreacted

starting materials. The resulting crystalline mass was then extracted with 200 ml. of hot hexane, and the extract evaporated under reduced pressure to give greenish-yellow crystals. It was recrystallized by dissolving in acetone and then slowly adding water, affording 0.6 g. yellow crystalline product.

Dichlorophenyl(tricarbonyltriphenylphosphinecobalt)tin(IV),

$\text{Cl}_2(\text{C}_6\text{H}_5)\text{SnCo}(\text{CO})_3\text{PPh}_3$: A mixture of 0.45 g. (1.05 mmole.) of $\text{Cl}_2(\text{C}_6\text{H}_5)\text{SnCo}(\text{CO})_4$ was mixed with 0.30 g. of PPh_3 and placed in a 10 ml. flask. It was heated to 100° for 10 minutes under vacuum during which time CO was rapidly evolved from the melt. The mixture was cooled and extracted with n-pentane to remove unreacted starting material. The crude solid material remaining was then crystallized by dissolving in 6 ml. benzene and slowly adding n-pentane. The first impure deposit produced during the initial stages of pentane addition was discarded. When 50 ml. of n-pentane had been added, the solution was cooled to 0° to allow the initially formed yellow needle-like crystals to grow. These crystals of product were then recrystallized by dissolving in acetone and slowly adding water. Yield 0.35 g.

Bis(acetylacetonato)bis(tetracarbonylcobalt)tin(IV),

$(\text{acac})_2\text{Sn}[\text{Co}(\text{CO})_4]_2$: A solution of 21.0 mmole. of $\text{NaCo}(\text{CO})_4$ in 50 ml. of THF was added dropwise from an addition funnel to a well-stirred solution of 7.8 g. (20.2 mmole.) of $(\text{acac})_2\text{SnCl}_2$

in 50 ml. of THF at room temperature. The addition was carried out over 1 1/2 hours (about 1 drop/2 sec.). When all the NaCo(CO)_4 solution had been added, the THF was removed under reduced pressure at room temperature, and the residue extracted by shaking with 100 ml. n-pentane in small portions. The extract was centrifuged and cooled to -80° when impure product was deposited as a dark red oily solid. The mother liquor was decanted from this material, evaporated to 10 ml. and cooled to -20° affording a further yield of product. The combined crude products were recrystallized three times by dissolving in the minimum quantity of n-pentane, centrifuging and cooling to -20° . This gave 0.5 g. of red-brown crystals of pure product.

Molecular weight calculated for $(\text{C}_5\text{H}_7\text{O}_2)_2\text{Sn}[\text{Co(CO)}_4]_2$: 658.9. Found in cyclohexane solution: 670^{+51} (1.07 mg./ml.) and 741^{+4} (27.2 mg./ml.).

Infrared spectrum in $\nu(\text{C}-\text{C})$ and $\nu(\text{C}-\text{O})$ region due to chelated acac groups: 1595(m), 1580(m), 1550(w), $1530(\text{ms.})\text{cm}^{-1}$.

Bis(acetylacetonato)heptacarbonyldicobalt tin(IV), $(\text{acac})_2\text{SnCo}_2(\text{CO})_7$: A solution of 22.2 mmole. of NaCo(CO)_4 in 50 ml. of THF was added rapidly (within a few minutes) to a vigorously stirred solution of $(\text{acac})_2\text{SnCl}_2$ in 50 ml. of THF at room temperature. After five minutes stirring, the THF was evaporated under reduced pressure at room temperature, and the residue extracted with n-pentane (c. 100 ml.).

After centrifuging and evaporating to 50 ml. the solution was cooled to -20° giving a deposit of dark oily crystals of impure product. The mother liquor was evaporated to 20 ml. and again cooled to -20° , this time affording 0.4 g. of $\text{ClSn}[\text{Co}(\text{CO})_4]_3$. Further evaporation of the mother liquor to 10 ml., followed by cooling to -80° , afforded a mixture of dark red oil and crystals, which, on further recrystallization by cooling an n-pentane solution to -20° , gave a further yield of impure product. Two recrystallizations of the combined crude products by cooling a saturated room temperature n-pentane solution to -20° afforded 0.85 g. of pure product as red crystals.

Molecular weight calculated for $(\text{C}_5\text{H}_7\text{O}_2)_2\text{SnCo}_2(\text{CO})_7$: 630.9. Found in cyclohexane solution 648 ± 4 (17.3 mg./ml.).

Infrared spectrum $\nu(\text{C-C})$ and $\nu(\text{C-O})$ region due to chelated acac group: 1595(m), 1580(m), 1565(W), 1530(m).

Effect of Mixing Rate on Reaction of $\text{NaCo}(\text{CO})_4$ and $\text{acac}_2\text{SnCl}_2$: To prove conclusively that the products of the reaction of $\text{Co}(\text{CO})_4^-$ with $\text{acac}_2\text{SnCl}_2$ are dependent on the rate of addition, two reactions were carried out keeping all conditions except mixing rate constant.

Solutions of 20 mmole. of $\text{NaCo}(\text{CO})_4$ in 50 ml. of THF and 20 mmole. of $\text{acac}_2\text{SnCl}_2$ in 50 ml. of THF were prepared, and both solutions divided into two equal volumes. The two halves of $\text{acac}_2\text{SnCl}_2$ solution were placed in 100 ml. round-bottomed flasks and stirred with magnetic stirrers at room temperature.

To flask 1, 25 ml. of $\text{NaCo}(\text{CO})_4$ solution was added rapidly (in less than two seconds) and stirred for five minutes. To flask 2, the remaining 25 ml. of $\text{NaCo}(\text{CO})_4$ solution was added dropwise from an addition funnel over the course of two hours. Both reaction mixtures were then worked up by removal of THF under reduced pressure, extraction of the residue with n-pentane, followed by concentration and cooling to -20° as described for the above preparations of acac derivatives. From reaction carried out in flask 1, 0.3 g. of $(\text{acac})_2\text{SnCo}_2(\text{CO})_7$ was obtained; while flask 2 afforded 0.3 g. of $(\text{acac})_2\text{Sn}[\text{Co}(\text{CO})_4]_2$.

Bis(acetylacetonato)chloro(tetracarbonylcobalt)tin(IV), $(\text{acac})_2\text{ClSnCo}(\text{CO})_4$: A solution of 9.3 mmole. of $\text{NaCo}(\text{CO})_4$ in 30 ml. of THF was added over the course of 15 minutes from an addition funnel to 6.1 g. (15.8 mmole.) of $\text{acac}_2\text{SnCl}_2$ in 50 ml. of the same solvent. The mixture was stirred at room temperature for 10 minutes, and the THF removed under reduced pressure. The residue was extracted with n-pentane, filtered and cooled to -20° affording a mixture of dark red needles of $\text{ClSn}[\text{Co}(\text{CO})_4]_3$, and yellow-orange crystals of product. The mixture of crystals was hand separated, and the product recrystallized twice from n-pentane affording 50 mg. of yellow crystals of product.

Infrared spectrum in the $\nu(\text{C-C})$ and $\nu(\text{C-O})$ region due to chelated acac group: 1595(m), 1580(m), 1565(w), 1530(s) cm^{-1} .

Dichlorobis(tetracarbonylcobalt)germanium(IV), $\text{Cl}_2\text{Ge}[\text{Co}(\text{CO})_4]_2$:

In an attempt to prepare $\text{ClGe}[\text{Co}(\text{CO})_4]_3$, 0.5 g. (2.3 mmole.) of GeCl_4 was dissolved in THF and added to 2.0 g. (5.9 mmole.) of $\text{Co}_2(\text{CO})_8$ in the same solvent stirred at room temperature. When the initial rapid CO evolution had ceased (about ten minutes), the THF was removed under reduced pressure, and the residue extracted with n-pentane. Filtration followed by evaporation to incipient crystallization and cooling to -80° afforded 0.8 g. of red crystals of $\text{Cl}_2\text{Ge}[(\text{CO})_4]_2$ which were recrystallized from n-pentane.

Reaction of SnCl_4 with $\text{Co}(\text{CO})_4^-$ in THF: In an attempt to prepare $\text{Cl}_3\text{SnCo}(\text{CO})_4$, a solution of 2.6 g. (10 mmole.) of SnCl_4 in 50 ml. of THF was stirred at room temperature and a solution of 5 mmole. of $\text{NaCo}(\text{CO})_4$ in 30 ml. of THF was added. After stirring for 10 minutes, the THF was removed under reduced pressure and the residue extracted with n-pentane. This was cooled to -20° affording 0.6 g. orange crystals of $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$. Evaporation of mother liquor to 8 ml., followed by cooling to -20° , gave 0.1 g. of dark red crystals of $\text{ClSn}[\text{Co}(\text{CO})_4]_3$. No $\text{Cl}_3\text{SnCo}(\text{CO})_4$ was obtained from the reaction.

Reaction of Tetravinyltin with $\text{Co}_2(\text{CO})_8$. (i) In THF Solution: A solution of 1.1 g. (4.8 mmole.) of tetravinyltin in THF was added to a stirred solution of 2.6 g. (7.6 mmole.) of $\text{Co}_2(\text{CO})_8$ in the same solvent. The solution was stirred

for 15 minutes during which time a small quantity of CO was evolved. THF was then removed under reduced pressure at room temperature on a rotary evaporator. During this process rapid gas evolution was observed. The residue was extracted with 100 ml. n-pentane, the extract evaporated to about 20 ml., and then cooled to -80° affording black crystals. These were dissolved in the minimum amount of pentane and cooled to -20° . Black crystals of impure $\text{Co}_4(\text{CO})_{12}$ (characterized by infrared) came down. The mother liquor was evaporated to about 5 ml. and cooled to -80° affording 0.3 g. of dark purple crystals which were recrystallized from n-pentane. They were characterized as $\text{CH}_3\text{C}[\text{Co}(\text{CO})_3]_3$ by infrared and mass spectrum.

(ii) In n-Pentane Solution: A solution of 2.3 g. (10 mmole.) of tetravinyltin and 3.4 g. (10 mmole.) of $\text{Co}_2(\text{CO})_8$ in 10 ml. of n-pentane was refluxed for one hour. The solution was then cooled to room temperature, centrifuged, and cooled to -80° for about a day. Crystals of $(\text{CH}_2\text{CH})_2\text{Sn}[\text{Co}(\text{CO})_4]_2$ came down and were recrystallized by dissolving in 8 ml. of n-pentane and cooling. A yield of 0.6 g. of product was obtained, and was a liquid at room temperature.

Effect of Heat on $\text{CH}_3\text{Sn}[\text{Co}(\text{CO})_4]_3$: (i) A 0.3 g. (4.6 mmole.) sample of $\text{CH}_3\text{Sn}[\text{Co}(\text{CO})_4]_3$ was sealed in an evacuated glass tube (0.5 cm. x 10 cm.) and heated to

80°-90° for one hour in an oil bath. The tube was then opened, and the contents dissolved in n-pentane. Cooling to -80° afforded 0.3 g. of unreacted starting material, characterized by infrared and melting point.

(ii) A toluene solution of 0.3 g. of $\text{CH}_3\text{Sn}[\text{Co}(\text{CO})_4]_3$ was refluxed for five hours. Complete decomposition to a metallic mirror and black insoluble material occurred.

Ultraviolet Irradiation of $\text{CH}_3\text{Sn}[\text{Co}(\text{CO})_4]_3$: A solution of 0.2 g. of $\text{CH}_3\text{Sn}[\text{Co}(\text{CO})_4]_3$ was dissolved in 25 ml. of n-hexane and irradiated with ultraviolet with stirring for 45 minutes. The solution became cloudy, and the infrared spectrum of the filtered solution showed that only starting material, $\text{Co}_4(\text{CO})_{12}$ and $\text{Co}_2(\text{CO})_8$ were present.

Tetrakis(tetracarbonylcobalt)tin(IV), $\text{Sn}[\text{Co}(\text{CO})_4]_4$: (i) A solution of 12.0 g. (35.1 mmole.) of $\text{Co}_2(\text{CO})_8$ in 50 ml. of THF was added to a solution of 2.6 g. (10.0 mmole). of SnCl_4 in 50 ml. of the same solvent, and the mixture stirred with a magnetic stirrer. The solution slowly evolved CO while being stirred at room temperature. After four hours very dark red crystals of product had been deposited, and were removed by filtration (yield; 1.8 g.). The filtrate was evaporated to 1/4 volume and stirred for 24 hours at room temperature. Filtration gave a further crop of 1.6 g. of product. The combined crude products were extracted with 250 ml. acetone which was filtered and evaporated to about 5 ml. affording

1.0 g. of very dark red glistening crystals of pure product. It could also be recrystallized in a similar fashion from n-pentane.

(ii) A solution of 2.6 g. (3.9 mmole.) of $\text{ClSn}[\text{Co}(\text{CO})_4]_3$ in 20 ml. of THF was added to 1.3 g. (3.8 mmole.) of $\text{Co}_2(\text{CO})_8$ in the same solvent. The mixture was stirred at room temperature for three hours during which time CO was slowly evolved.

The solution was then filtered from precipitated crystals of product (0.6 g.) and the filtrate stirred for a further 12 hours. This gave a further crop of crystals (2.0 g.) which was removed by filtration. The combined crude products were crystallized by evaporation of a solution in a large volume of n-pentane to a small volume. This afforded a yield of 1.5 g.

Molecular weight calculated for $\text{Sn}[\text{Co}(\text{CO})_4]_4$: 802.6.
Found in cyclohexane solution: 880 ± 100 (1.36 mg./ml.).

CHAPTER III

A. Syntheses of Tetracarbonylcobalt Derivatives of Gallium, Indium and Thallium

INTRODUCTION

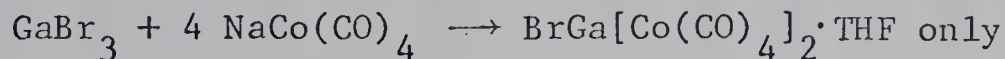
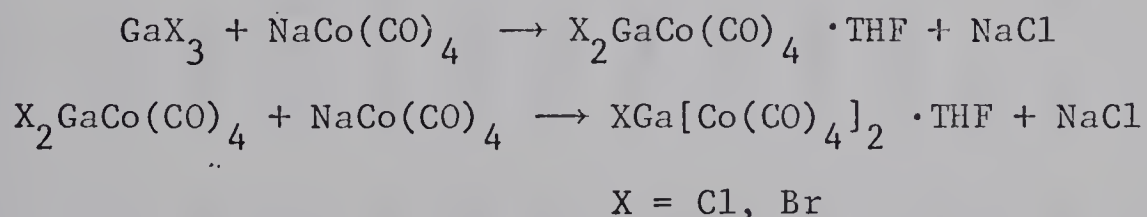
The first report of tetracarbonylcobalt derivatives of group III metals appeared in 1942 when Hieber and Teller (9) described the preparation of $\text{In}[\text{Co}(\text{CO})_4]_3$, $\text{TlCo}(\text{CO})_4$ and $\text{Tl}[\text{Co}(\text{CO})_4]_3$. These were made by treating a mixture of finely divided group III metal, and either cobalt metal, or cobalt bromide, with carbon monoxide at a pressure of several hundred atmospheres, and a temperature of several hundred degrees. They were unable to isolate any gallium derivatives using this technique. They suggested that the $\text{Co}(\text{CO})_4$ groups were bonded to the group III metal by CO bridges, as was discussed in Chapter I. It is now realized that these derivatives involve direct covalent bonds between cobalt and the group III metal. Since this paper appeared, there have been no reports of other tetracarbonylcobalt derivatives of group III metals, although in 1956 Hieber and Breu reported some triphenylphosphine substituted derivatives such as $\text{Tl}[\text{Co}(\text{CO})_3\text{PPh}_3]_3$ (12). It was therefore decided to investigate the synthesis of further tetracarbonylcobalt derivatives of indium, and to extend these studies to gallium.

RESULTS AND DISCUSSION

The syntheses discussed in this section involve displacement of halide ions from indium, gallium and thallium halides. The compounds prepared are listed in Table VI which also includes analytical data, melting points and colours. The preparation of some of these derivatives by insertion reactions is discussed in Chapter IV.

1. Synthesis of Gallium Derivatives

These were prepared by displacing halide ion from gallium trihalides with NaCo(CO)_4 in THF solution at room temperature. Both mono- and bis(tetracarbonylcobalt) derivatives of gallium were synthesized by this method, however, attempts to prepare $\text{Ga[Co(CO)}_4\text{]}_3$ by displacing the third halogen were unsuccessful, even when NaCo(CO)_4 was in considerable excess:



In this respect gallium closely resembles germanium. Treatment of organogermanium trihalides with excess Co(CO)_4^- resulted in displacement of no more than two halogens.

Acetylacetonate derivatives were prepared by treatment of one mole of either $\text{Br}_2\text{GaCo(CO)}_4 \cdot \text{THF}$ or $\text{BrGa[Co(CO)}_4\text{]}_2 \cdot \text{THF}$ with one mole of thallium (I) acetylacetonate:

TABLE VI

Analytical Data, Colours and Melting Points of Group III and V Derivatives

Compound	M.p. °C	Colour	Calculated %			Found %				
			C	H	O	X	C	H	O	X
Cl ₂ GaCo(CO) ₄ ·THF	56-60	White	25.1	2.1	20.9	18.5	24.7	2.1	20.1	19.0
Br ₂ GaCo(CO) ₄ ·THF ^a	82-87	Pale Yellow	20.3	1.7	16.9	33.8	19.3	1.8	15.1	34.3
Br(acac)GaCo(CO) ₄	65-68	Pale Yellow	25.8	1.7	22.9	19.1	25.6	2.0	21.2	19.8
ClGa[Co(CO) ₄] ₂ ·THF ^b	66-70	Yellow	27.8	1.6	27.8	6.9	26.0	1.7	25.8	7.5
BrGa[Co(CO) ₄] ₂ ·THF	82-85	Yellow	25.6	1.4	25.6	14.2	24.2	1.1	24.3	14.9
(acac)Ga[Co(CO) ₄] ₂	51-53	Yellow	30.6	1.4	31.3	0.0	29.1	1.2	30.9	0.0
BrIn[Co(CO) ₄] ₂ ·THF	72-75	Yellow	23.7	1.3	-	13.1	23.4	1.1	-	13.9
BrIn[Co(CO) ₄] ₂ ^c	140-150	Orange	17.9	0.0	23.8	14.8	17.7	0.1	23.8	15.1
(acac)In[Co(CO) ₄] ₂	28-32	Yellow	28.0	1.4	28.0	-	28.1	1.6	29.1	-
In[Co(CO) ₄] ₃	92-94	Red	23.0	0.0	30.6	0.0	22.1	1.3	27.7	0.0
Tl[Co(CO) ₄] ₃ ^d	61-65	Dark Red	20.1	0.0	26.8	-	20.4	0.2	25.2	-

TABLE VI (continued)

Compound	M.p. °C	Colour	Calculated %			Found %				
			C	H	O	X	C	H	O	X
$\text{Br}_2\text{SbCo}(\text{CO})_3\text{PPh}_3^{\text{e}}$	dec 120	Brown	36.8	2.2	-	23.2	36.7	2.3	-	20.2
$\text{Bi}[\text{Co}(\text{CO})_4]_3^{\text{f}}$	Dec 94	Black	19.9	0.0	26.6	-	19.6	0.0	26.8	-
$\text{BiCo}_3(\text{CO})_{10}^{\text{g}}$	Dec 130	Dark green	18.0	0.0	24.0	-	18.0	0.4	25.2	-

^a Ga: Calculated, 14.7; Found, 14.2. Co: Calculated, 12.4; Found, 15.7

^b Ga: Calculated, 13.5; Found, 14.3. Co: Calculated, 22.7; Found, 23.8

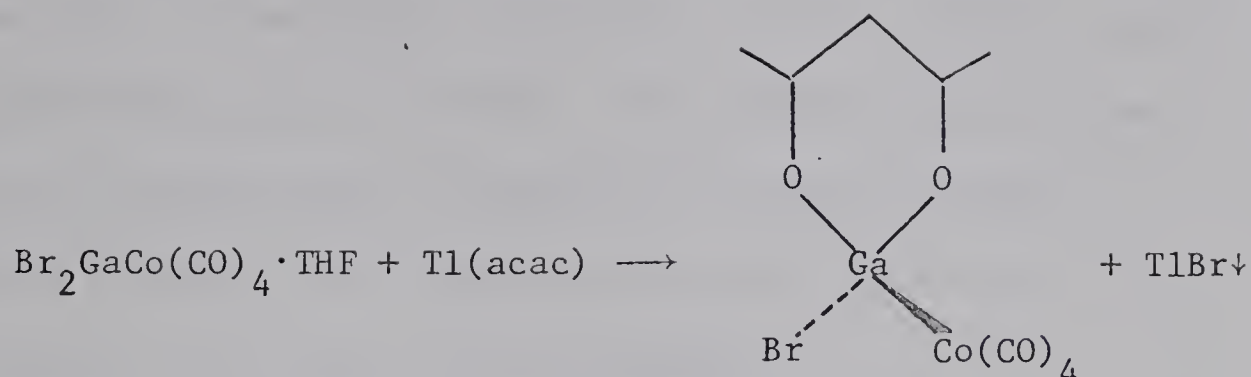
^c In: Calculated, 21.4; Found, 23.9. Co: Calculated, 21.9; Found, 18.9.

^d Co: Calculated, 24.7; Found, 24.2.

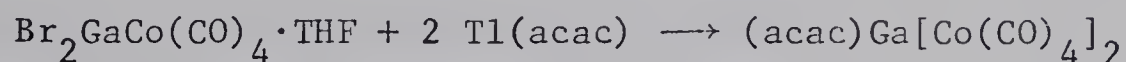
^e P: Calculated, 4.5; Found, 4.1.

^f Bi: Calculated, 28.9; Found, 28.5. Co: Calculated, 24.5; Found, 23.6.

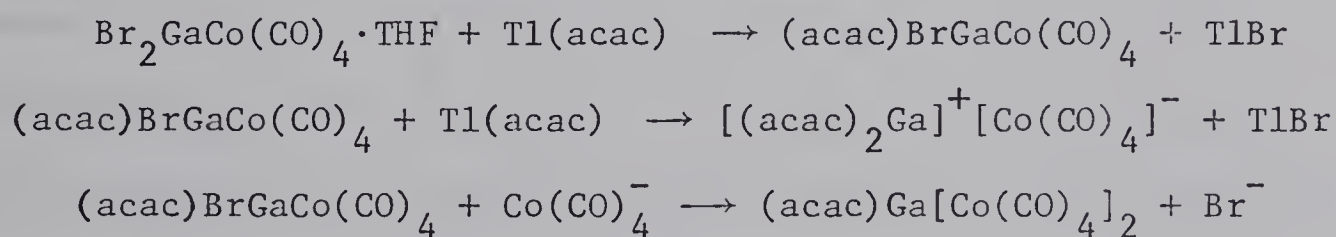
^g Bi: Calculated, 31.4; Found, 30.6. Co: Calculated, 26.5; Found, 26.5.



Treatment of $\text{Br}_2\text{GaCo(CO)}_4 \cdot \text{THF}$ with two moles of Tl(acac) , however, resulted in disproportionation with formation of $(\text{acac})\text{Ga[Co(CO)}_4\text{]}_2$ rather than $(\text{acac})_2\text{GaCo(CO)}_4$:



A reaction sequence that would account for this product might involve the initial formation of $(\text{acac})\text{BrGaCo(CO)}_4$, followed by its reaction with a second mole of Tl(acac) to release Co(CO)_4^- , this could then attack unreacted $(\text{acac})\text{BrGaCo(CO)}_4$ to give the observed product:



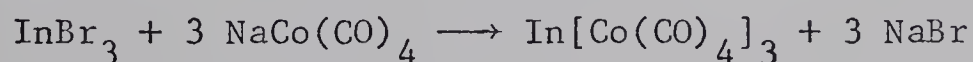
This reaction scheme would also involve the formation of $[(\text{acac})_2\text{Ga}]\text{Br}$, and in fact a small quantity of a white crystalline material was isolated in addition to the main product. On the basis of its infrared spectrum, this compound was found to possess acac groups but no Co(CO)_4 groups.

All of the gallium derivatives prepared were white to yellow, very air sensitive crystalline solids, and were soluble in polar and non-polar solvents. The chloro derivatives were also very deliquescent; on exposure to air they rapidly absorbed moisture with formation of an oily liquid and development of a strong odour of $\text{HCo}(\text{CO})_4$.

With the exception of the acetylacetonate derivatives, all the compounds prepared possessed THF coordinated to gallium. These adducts were quite stable, and could be sublimed in vacuo at 40° without any loss of THF. Gallium thus retains strong acceptor properties when bonded to cobalt.

2. Synthesis of Indium and Thallium Derivatives

By treatment of InBr_3 with two and three moles of $\text{NaCo}(\text{CO})_4$ in THF, both $\text{BrIn}[\text{Co}(\text{CO})_4]_2 \cdot \text{THF}$ and $\text{In}[\text{Co}(\text{CO})_4]_3$ were prepared:



However, attempts to replace only one Br^- were not successful, $\text{BrIn}[\text{Co}(\text{CO})_4]_2 \cdot \text{THF}$ being formed. The bromo derivative formed yellow moderately air sensitive needles which lost THF completely in vacuo at room temperature over the course of 24 hours. The loss in weight corresponded to loss of one mole of THF per mole of compound. The product, $\text{BrIn}[\text{Co}(\text{CO})_4]_2$, an orange crystalline material, was insoluble in such solvents as n-pentane and cyclohexane, and only slightly soluble in benzene from which it was recrystallized by concentration of a saturated solution. It is

perhaps dimeric, or polymeric, with bromine bridges between the indium atoms. The relative instability of the THF adduct of $\text{BrIn}[\text{Co}(\text{CO})_4]_2$ compared to that of the gallium analogue is consistent with the greater electronegativity of the latter metal.

By treatment with $\text{Tl}(\text{acac})$, $\text{BrIn}[\text{Co}(\text{CO})_4]_2 \cdot \text{THF}$ was converted to the acetylacetonato derivative $(\text{acac})\text{In}[\text{Co}(\text{CO})_4]_2$, a bright yellow crystalline material with a low melting point (28°).

Treatment of TlCl_3 with 3 moles of $\text{NaCo}(\text{CO})_4$ afforded the fully substituted derivative, $\text{Tl}[\text{Co}(\text{CO})_4]_3$, as deep red (almost black) crystals. It was air sensitive and was soluble in non-polar solvents such as n-pentane. This compound was originally prepared by Hieber and Teller (9) using high pressure techniques.

B. Synthesis of Cobalt Carbonyl Derivatives of Antimony and Bismuth

INTRODUCTION

Compounds in which transition elements are covalently bonded to group V elements are not very numerous, (excluding those in which the group V atom is acting solely as an electron pair donor). Such compounds include $(\text{CF}_3)_2\text{AsMo}(\text{CO})_3\text{Cp}$ (117), $\text{Ph}_2\text{BiRe}(\text{CO})_5$ (26), and the somewhat obscure substances $\text{AsFe}_3(\text{CO})_{11}$, $\text{SbFe}(\text{CO})_4$ and $\text{Bi}_2\text{Fe}_5(\text{CO})_{20}$ (30). Recently some compounds with cobalt-group V bonds were reported by Schrauzer and Kratel (35). They described the preparation of $\text{Ph}_2\text{SbCo}(\text{D}_2\text{H}_2)\text{Py}$ and $\text{Ph}_2\text{BiCo}(\text{D}_2\text{H}_2)\text{Py}$ (where D = the dianion of dimethylglyoxime and Py = pyridine) as stable crystalline materials. Earlier, Hayter (118) had reported some phosphorous bridged compounds such as $[\text{Ph}_2\text{PCo}(\text{CO})_3]_2$, but the only report so far of a tetracarbonylcobalt derivative is that by Baay and MacDiarmid (119) who prepared $\text{Me}_2\text{AsCo}(\text{CO})_4$. This compound was unstable and decomposed to the dimeric compound $[\text{Me}_2\text{AsCo}(\text{CO})_3]_2$ in which arsenic bridges the two cobalt atoms.

In an attempt to prepare tetracarbonylcobalt derivatives of antimony and bismuth, the reaction of cobalt carbonyl with trihalides of these elements was investigated.

RESULTS AND DISCUSSION

Analytical data for compounds discussed in this section are given in Table VI.

By treating antimony tribromide with cobalt carbonyl in n-pentane solution, a red crystalline compound was formed. It was unstable at room temperature, even under nitrogen, but could be stored without appreciable decomposition at -80° . Owing to this instability, meaningful analytical results could not be obtained. The infrared spectrum of this compound in the carbonyl stretching region, however, possessed 4 strong bonds characteristic of mono(tetracarbonylcobalt) derivatives with C_s symmetry (see Chapter V). This compound was therefore tentatively formulated as $Br_2SbCo(CO)_4$. Confirmation of this was obtained by converting this compound to the much more stable triphenylphosphine derivative which was characterized as $Br_2SbCo(CO)_3PPh_3$ by elemental analysis. The infrared spectrum in the carbonyl stretching region (Figure 20, Chapter V) was similar to other C_s $Co(CO)_3PPh_3$ derivatives, such as $PhCl_2SnCo(CO)_3PPh_3$, and was thus consistent with this structure. The PPh_3 derivative was readily prepared by treatment of $Br_2SbCo(CO)_4$ with PPh_3 in methylene chloride solution at 0° :

$$4SbBr_3 + 3Co_2(CO)_8 \longrightarrow 4Br_2SbCo(CO)_4 + 2CoBr_2 + 8 CO$$

$$Br_2SbCo(CO)_4 + PPh_3 \longrightarrow Br_2SbCo(CO)_3PPh_3 + CO$$

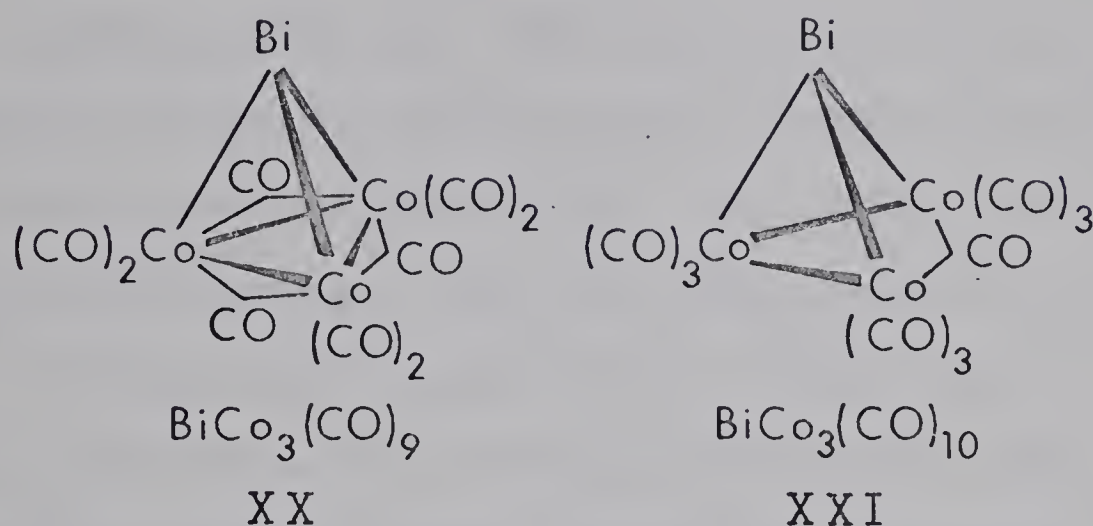
This derivative was much more stable than the tetracarbonyl compound towards both thermal decomposition and atmospheric

oxidation.

Attempts to carry out an analogous reaction with BiI_3 resulted in complete substitution. Reaction of BiI_3 with $\text{Co}_2(\text{CO})_8$ in THF or pentane solution gave a black crystalline very air sensitive material characterised as $\text{Bi}[\text{Co}(\text{CO})_4]_3$ by total elemental analysis. This was confirmed by its mass spectrum which possessed a peak at $m/e = 722$ due to the parent ion $\text{BiCo}_3(\text{CO})_{12}^+$. Its molecular weight in cyclohexane was 805 (calculated: 722), however little reliance can be placed on this figure due to decomposition in solution.

In one reaction in which excess BiI_3 was employed, a different product was obtained. Subsequent investigation showed that the same product was also obtained when $\text{Bi}[\text{Co}(\text{CO})_4]_3$ was treated with BiI_3 in pentane solution. The compound produced in these reactions formed very dark green, air sensitive needles. Its infrared spectrum in the carbonyl stretching region (Figure 41, Chapter V) showed 4 bands due to terminal carbonyl groups, and one, at 1882 cm^{-1} , assigned to a bridging carbonyl. The highest fragment observed in the mass spectrum had an m/e value of 638 corresponding to $\text{BiCo}_3(\text{CO})_9^+$, and the determination of the exact mass of the $m/e = 386$ peak proved this fragment to be BiCo_3^+ . However, a total elemental analysis agreed closely with $\text{BiCo}_3(\text{CO})_{10}$, although differences between the calculated analytical data for $\text{BiCo}_3(\text{CO})_9$ and $\text{BiCo}_3(\text{CO})_{10}$ are very slight. Two of

the structures consistent with the above experimental findings are shown in XX and XXI, while a third possibility is $(\text{CO})_4\text{CoBiCo}_2(\text{CO})_7$ (XXII), a structure related to that of $\text{Co}_2(\text{CO})_8$ by replacing one CO bridge by a bismuth bridge.



Structure XX has C_{3v} symmetry for which a maximum of three terminal (A_1+2E) and two bridging (A_1+E) infrared active CO stretching frequencies are predicted. As the observed spectrum consists of 4 strong terminal, and one strong bridging carbonyl stretching frequency, the structure XX can be tentatively rejected. However, it is not possible to decide between XXI and XXII in this way. They both possess C_s symmetry for which a maximum of nine or ten terminal terminal CO bands ($5A'+4A''$, or $6A'+4A''$), and one bridging CO bond for each, is predicted. More definite conclusions regarding the structure of this compound must therefore await an X-ray structural determination which is at present being conducted by Professor L.F. Dahl and co-workers.

EXPERIMENTAL

This section describes the preparation of compounds discussed in Parts A and B. Reagents and general procedures are the same as described in Chapter II.

Starting Materials

Gallium trichloride: This was prepared by the reaction of chlorine on metallic gallium, and is a modification of the method outlined by Brauer (120). The reaction vessel consisted of a horizontal glass tube with a U-bend at one end, the arms of the U being vertical. Gallium metal was placed in the bottom of the U-bend, and was gently heated to melt the gallium. Chlorine was then passed down the short arm of the U by means of a gas inlet tube, so that the gas bubbled through the molten metal. During this process, crystals of GaCl_3 were deposited on the walls of the long horizontal tube. When all of the gallium had reacted, the product was distilled to the far end of the tube in a stream of nitrogen. The pure product was then transferred to a stoppered bottle and stored under nitrogen until needed.

Gallium tribromide: This was prepared by the procedure described by Brauer (121). A 100 ml. three-necked pear-shaped flask was fitted with a reflux condenser and a gas inlet tube which reached nearly to the bottom of the flask. The flask was then charged with 30g. of metallic gallium,

and heated to melt the metal. A stream of nitrogen was then first bubbled through a washbottle containing bromine, and then through the molten gallium via the gas inlet tube. A clear melt of GaBr_3 formed on the surface of the gallium, and turned red due to dissolved bromine when all the gallium had reacted. At the end of the reaction, pure nitrogen was bubbled through the melt for about 15 minutes to remove much of the excess bromine. The product was then purified by distillation into a receiver in the same nitrogen stream. The boiling point of GaBr_3 is 279° . It was stored under nitrogen.

Indium tribromide: This was prepared by dissolving metallic indium in 48% hydrobromic acid. Although the initial reaction was quite vigorous, heating was eventually required. When no more indium would dissolve, the solution was decanted from excess metal into an evaporating basin, and evaporated to dryness on a hot plate, the temperature of the solution being kept above 33° . The product was then dried by warming in vacuo for two to three days. It was used without further purification.

Preparation of Tetracarbonylcobalt Derivatives

Dichloro(tetracarbonylcobalt)gallium(III) tetrahydrofuranate,

$\text{Cl}_2\text{GaCo}(\text{CO})_4 \cdot \text{THF}$: A solution of 10.0 mmole. of $\text{NaCo}(\text{CO})_4$ in THF was added to a stirred, room temperature solution of 1.0 g. (5.7 mmole.) of GaCl_3 in the same solvent. After stirring for

10 minutes, the solvent was removed under reduced pressure, and the residue extracted with about 150 ml. of n-pentane. This extract was filtered and cooled in Dry Ice until no more crystals were deposited. Four recrystallizations from n-pentane were necessary to free the product from a yellow impurity which was presumed to be the disubstituted product. Yield of pure product was 0.1 g.

Chlorobis(tetracarbonylcobalt)gallium(III) tetrahydrofuranate, $\text{ClGa}[\text{Co}(\text{CO})_4]_2 \cdot \text{THF}$: A solution of 1.76 g. (10.0 mmole.) of GaCl_3 in 50 ml. of THF was added to 20.0 mmole. of $\text{NaCo}(\text{CO})_4$ in the same solvent, and the mixture stirred at room temperature for 15 minutes. The solvent was then evaporated under reduced pressure, and the oily residue extracted with 60 ml. of n-pentane. The extract was evaporated until crystals began to form, and then cooled in Dry Ice. The crude product so produced was twice recrystallized from n-pentane at -80° , affording 1.3 g. of lemon-yellow crystals of pure product.

Dibromo(tetracarbonylcobalt)gallium(III) tetrahydrofuranate, $\text{Br}_2\text{GaCo}(\text{CO})_4 \cdot \text{THF}$: A solution of 3.09 g. (10.0 mmole.) of GaBr_3 in THF was stirred at room temperature, and a THF solution of 10 mmole. of $\text{NaCo}(\text{CO})_4$ added. After stirring for five minutes, THF was removed under reduced pressure and the residue extracted with n-pentane. The extract was evaporated until crystals began to form and was then cooled to -80° producing 4.1 g. of crude product. This was taken

up in the minimum amount of n-pentane and cooled to -80° in a Dry Ice/acetone bath affording pale yellow crystals of product.

Bromobis(tetracarbonylcobalt)gallium(III) tetrahydrofuranate, $\text{BrGa}[\text{Co}(\text{CO})_4]_2 \cdot \text{THF}$: A THF solution of 11.0 mmole. of $\text{NaCo}(\text{CO})_4$ was added to 4.6 g. (9.7 mmole.) of $\text{Br}_2\text{GaCo}(\text{CO})_4 \cdot \text{THF}$ in the same solvent. The mixture was stirred at 0° in an ice bath for 10 minutes. The THF was then removed under reduced pressure and the residue extracted with 100 ml. of n-pentane. The extract was cooled to -80° in Dry Ice and the crystals so produced were recrystallized from n-pentane affording a 60% yield of lemon-yellow needles of product.

Reaction of GaBr_3 with $3 \text{Co}(\text{CO})_4^-$: A solution of 1.5 g. (4.85 mmole.) of GaBr_3 in 40 ml. of THF was added to a solution of 20.0 mmole. of $\text{NaCo}(\text{CO})_4$ in 50 ml. of the same solvent, and the mixture stirred at room temperature for 15 minutes. Solvent was removed under reduced pressure, and the residue extracted with 150 ml. of n-pentane. The extract was cooled to -80° affording oily crystals. Three recrystallizations from n-pentane at -80° gave 1.2 g. of pure yellow crystals of $\text{BrGa}[\text{Co}(\text{CO})_4]_2 \cdot \text{THF}$, characterized by comparison of infrared spectrum and melting point with those of an authentic sample.

Bromo(acetylacetonato)(tetracarbonylcobalt)gallium(III), $(\text{acac})\text{BrGaCo}(\text{CO})_4$: Thallium (I) acetylacetonate (1.0 g.,

3.3 mmole.) in THF was added to a well-stirred solution of 1.6 g. (3.4 mmole.) of $\text{Br}_2\text{GaCo}(\text{CO})_4 \cdot \text{THF}$ in the same solvent. The precipitated TlBr was removed, the solution evaporated to dryness, and the residue extracted with n-pentane. Evaporation of the extract to a very small volume (about 0.5 ml.) and cooling in Dry Ice deposited star-shaped crystals. These were recrystallized from n-pentane at -80° affording pure product as pale yellow plates in 25% yield.

(Acetylacetonato)bis(tetracarbonylcobalt)gallium(III),

(acac)Ga[Co(CO) $_4$] $_2$: (i) A stirred solution of 0.6 g. (1.06 mmole.) of $\text{BrGa}[\text{Co}(\text{CO})_4]_2 \cdot \text{THF}$ in 20 ml. of THF was cooled to 0°C in an ice bath. A solution of 0.35 g. (1.03 mmole.) of $\text{Tl}(\text{acac})$ in THF was then slowly added. The solution turned purple, and a white precipitate of TlBr was formed. The solution was then filtered, evaporated to dryness, and extracted with n-pentane. On evaporating the extract to a small volume and cooling in Dry Ice, pale yellow crystals were deposited. Recrystallization from n-pentane at -80° afforded pure product.

(ii) A solution of $\text{Tl}(\text{acac})$ (1.28 g. 4.2 mmole.) in THF was added dropwise to a stirred solution of 1.0 g. (2.12 mmole.) of $\text{Br}_2\text{GaCo}(\text{CO})_4 \cdot \text{THF}$ in the same solvent at 0° . Precipitated TlBr was removed by filtration, and the solvent removed under reduced pressure. The residue was extracted with n-pentane, and the extract evaporated to a

small volume causing deposition of small white glistening crystals. The infrared spectrum of these crystals indicated the presence of chelated acetylacetonate groups (1590 cm^{-1} , 1535 cm^{-1}) but no $\text{Co}(\text{CO})_4$ groups, and they were probably $(\text{acac})_2\text{GaBr}$. After removal of these crystals, the pentane solution was evaporated to dryness in vacuo giving a brown oil which set to a mass of crystals. These were redissolved in the minimum of n-pentane and cooled to -80° affording pale yellow crystals of product in a 0.1 g. yield after recrystallization.

Bromobis(tetracarbonylcobalt)indium(III)tetrahydrofuranate, $\text{BrIn}[\text{Co}(\text{CO})_4]_2 \cdot \text{THF}$: A solution of 11.0 mmole. of $\text{NaCo}(\text{CO})_4$ in THF was added to a stirred solution of 1.77 g. (5.0 mmole.) of InBr_3 in 50 ml. of the same solvent at room temperature. After 10 minutes stirring the THF was removed at reduced pressure, and the residue extracted with n-pentane. The combined extracts were evaporated to incipient crystallization and cooled in Dry Ice affording 1.7 g. of product which was recrystallized once from n-pentane at -80° .

Molecular weight calculated for $\text{BrIn}[\text{Co}(\text{CO})_4]_2 \cdot \text{THF}$: 608.7. Found in benzene solution: 607.

Bromobis(tetracarbonylcobalt)indium(III), $\text{BrIn}[\text{Co}(\text{CO})_4]_2$:
This was prepared by subjecting a 0.6075 g. sample of $\text{BrIn}[\text{Co}(\text{CO})_4]_2 \cdot \text{THF}$ to a vacuum of 20 microns for 24 hours. After this time the sample possessed a constant weight, the

percentage weight loss (12.2%) corresponding to loss of one mole of THF per molecule (THF calculated for $\text{BrIn}[\text{Co}(\text{CO})_4]_2 \cdot \text{THF} = 11.8 \%$). The yellow-orange powder thus produced was dissolved in 200 ml. of benzene, the solution filtered and then evaporated under reduced pressure to about 5 ml. affording light orange crystals of pure product.

Molecular weight calculated for $\text{BrIn}[\text{Co}(\text{CO})_4]_2 = 536.6$.

Found in acetone solution: 508.

(Acetylacetonato)bis(tetracarbonylcobalt)indium(III),

(acac)In[Co(CO)₄]₂: Thallium (I) acetylacetonate (1.5 g. 5.0 mmole.) in THF was added to 3.0 g. (4.95 mmole.) of $\text{BrIn}[\text{Co}(\text{CO})_4]_2 \cdot \text{THF}$ in the same solvent, stirred at room temperature. The solution was filtered, evaporated to dryness, and extracted with n-pentane. The extract, on cooling to -80° , gave 2.0 g. of yellow crystals, which on recrystallization from 8 ml. of n-pentane at -80° afforded 1.5 g. of pure product.

Tris(tetracarbonylcobalt)indium(III), In[Co(CO)₄]₃:

A solution of 1.7 g. (4.8 mmole.) of InBr_3 in THF was added to 17.0 mmole. of $\text{NaCo}(\text{CO})_4$ in the same solvent. After stirring for 10 minutes at room temperature, the THF was removed under reduced pressure, and the residue extracted with n-pentane. Cooling this solution to -80° afforded red crystals of product in 30% yield (after recrystallization).

Tris(tetracarbonylcobalt)thallium(III), $\text{Tl}[\text{Co}(\text{CO})_4]_3$:

A solution of 1.0 g. (3.2 mmole.) of TlCl_3 in THF was added to a well-stirred solution of 10 mmole. of $\text{NaCo}(\text{CO})_4$ in the same solvent. After removal of solvent under reduced pressure, the residue was extracted with n-pentane. Cooling the extract to -80° deposited very deep red (almost black) crystals of product in 40% yield.

Dibromo(tetracarbonylcobalt)antimony(III), $\text{Br}_2\text{SbCo}(\text{CO})_4$:

Finely divided SbBr_3 (3.6 g., 10 mmole.) was suspended in 50 ml. of n-pentane and stirred at room temperature. On addition of 2.5 g. (13.6 mmole.) of $\text{Co}_2(\text{CO})_8$, rapid CO evolution occurred, and a dark green solid was deposited. After 20 minutes the solution was centrifuged and the red solution cooled to -80° affording red crystals of crude product. Recrystallization from n-pentane at -80° afforded 1.2 g. of red needles of product slightly contaminated with decomposed material. Completely pure product could not be obtained owing to rapid decomposition at room temperature of both solid and solution.

Dibromo(triphenylphosphinetricarbonylcobalt)antimony(III),

$\text{Br}_2\text{SbCo}(\text{CO})_3\text{PPh}_3$: A solution of 0.45 g. (1.0 mmole.) of freshly prepared $\text{Br}_2\text{SbCo}(\text{CO})_4$ in 10 ml. of dichloromethane was cooled to 0° in an ice bath. To this 0.3 g. (1.1 mmole.) of PPh_3 was added causing CO to be evolved. After stirring at 0° for 15 minutes the solution was centrifuged and n-pentane added slowly. After the first 15 ml. had been added the

dirty brown impure material so formed was rejected and a further 70 ml. of n-pentane added. After cooling to -20° , 0.15 g. of sparkling brown crystals of product were obtained. Attempts to purify it further were not successful owing to decomposition in solution.

Tris(tetracarbonylcobalt)bismuth(III), $\text{Bi}[\text{Co}(\text{CO})_4]_3$:

A suspension of 6.0 g. (10.2 mmole.) of powdered BiI_3 was stirred at room temperature with 7.6 g. (22.2 mmole.) of $\text{Co}_2(\text{CO})_8$ in 50 ml. of n-pentane. After 22 hours the solution was centrifuged and cooled to -20° affording shining black crystals. These were recrystallized from n-pentane at -20° giving a yield of 0.7 g. of pure product.

Molecular weight calculated for $\text{Bi}[\text{Co}(\text{CO})_4]_3$: 721.89.
Found in cyclohexane solution 805 ± 11 (5.72 g./l.).

Decacarbonyltricobaltbismuth(III), $\text{BiCo}_3(\text{CO})_{10}$ (?) :

A suspension of 3.0 g. (5.1 mmole.) of BiI_3 in an n-pentane solution of 3.8 g. (11.1 mmole.) of $\text{Co}_2(\text{CO})_8$ was stirred at room temperature for 20 hours. At the end of this period the infrared spectrum showed bands due to $\text{Bi}[\text{Co}(\text{CO})_4]_3$ only. The solution was then centrifuged, and stirred at room temperature with a further 3.0 g. of powdered BiI_3 . After 20 hours the solution was again centrifuged and evaporated to about 10 ml. Cooling to -20° afforded very dark green crystals which were recrystallized from n-pentane to give a yield of 0.8 g. of pure product as extremely fine needle-

like crystals.

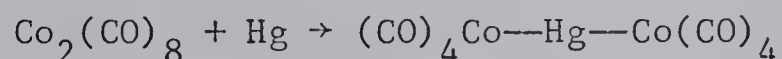
CHAPTER IV

A. A Study of Insertion Reactions of Transition Metal-Metal Bonds

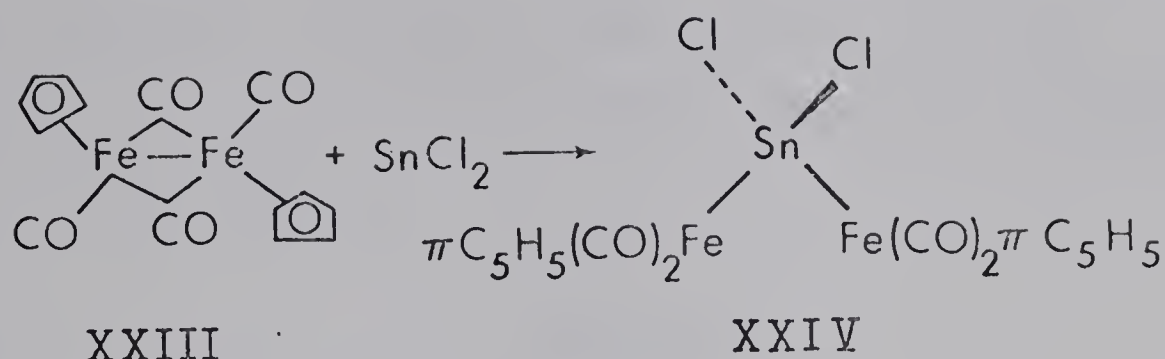
INTRODUCTION

It has recently been observed that certain derivatives of main group metals in lower oxidation states, (e.g. SnCl_2), will react with such transition metal complexes as $\text{Co}_2(\text{CO})_8$ and $[\text{Fe}(\text{CO})_2\text{Cp}]_2$ which possess metal-metal bonds. The products of these reactions are compounds in which the main group metal atom has inserted itself between the two transition metals giving two main-transition metal bonds. These reactions are thus referred to as insertion reactions, but this term is not intended to possess any mechanistic implications.

The first reported insertion reaction appears to be that of Dighe and Orchin (97) who treated $(\text{CO})_4\text{CoFe}(\text{CO})_2\text{Cp}$ with mercury for several days, and isolated $(\text{CO})_4\text{CoHgFe}(\text{CO})_2\text{Cp}$. In this reaction mercury inserted into the $\text{Co}-\text{Fe}$ bond. A very similar reaction of Hg with $\text{Co}_2(\text{CO})_8$ was later reported by the same authors (89):



In 1964 Bonati and Wilkinson (19) carried out a similar reaction with stannous chloride and $[\text{Fe}(\text{CO})_2\text{Cp}]_2$ (XXIII), and obtained $\text{Cl}_2\text{Sn}[\text{Fe}(\text{CO})_2\text{Cp}]_2$ (XXIV) a compound with two tin-iron bonds:



Germanium diiodide reacted in the same way giving $\text{I}_2\text{Ge}[\text{Fe}(\text{CO})_2\text{Cp}]_2$ (81).

Very recently Ruff (122) was able to react SnI_2 and GeI_2 with the dinuclear anionic species $\text{Cr}_2(\text{CO})_{10}^{2-}$ and $\text{W}_2(\text{CO})_{10}^{2-}$ with the formation of $[\text{I}_2\text{SnM}_2(\text{CO})_{10}]^{2-}$ and $[\text{I}_2\text{GeM}_2(\text{CO})_{10}]^{2-}$. These reactions were believed to involve insertion of Ge or Sn into the transition metal-metal bonds assumed to be present in the anions.

The main group derivatives SnCl_2 , SnI_2 , GeI_2 and Hg, involved in the above insertion reactions, are examples of a class of compounds sometimes referred to as carbenoids. This term has been applied to compounds of elements whose valence electron shells bear a formal similarity to those of carbenes (divalent carbon derivatives such as $:\text{CH}_2$). A carbenoid can be defined as a species which possesses at least one nonbonding electron pair, and at least one vacant p orbital, but must not have any vacant d orbitals with a main quantum number lower than the valence shell. This definition was given by Volpin et al. (123)

and by Nefedov and Mankov who also discussed in detail the general chemistry of carbenoids (124). Species which satisfy these conditions are listed in Table VII, but only those inside the box are capable of indefinite independent existence under normal conditions.

TABLE VII

II	III	IV	V	VI
$\begin{array}{c} \text{O} \\ \vdots \text{E} \text{O} \\ \text{O} \end{array}$	$\begin{array}{c} \text{O} \\ \vdots \text{EX} \\ \text{O} \end{array}$	$\begin{array}{c} \text{O} \\ \vdots \text{EX}_2 \\ \text{O} \end{array}$	$\begin{array}{c} \text{O} \\ \vdots \text{EX} \\ \text{O} \end{array}$	$\begin{array}{c} \text{O} \\ \vdots \text{E} \vdots \end{array}$
Be	BX	CX ₂	NX	O
Mg	AlX	SiX ₂	PX	S
Zn	GaX	GeX ₂	AsX	Se
Cd	InX	SnX ₂	SbX	Te
Hg	TlX	PbX ₂	BiX	Po

For a species to undergo an insertion reaction, it must fulfil at least two conditions, (a) it must be capable of increasing its oxidation and coordination number by two units, and (b) it must form stable bonds with transition metals. The first condition is satisfied by all the carbenoids listed in Table VII, it might therefore be expected that carbenoids in general would insert into transition metal-metal bonds, providing the second condition is fulfilled. In order to test this hypothesis, the following investigations of the reactions of carbenoids with Co₂(CO)₈ and other dinuclear species was undertaken.

RESULTS AND DISCUSSION

1. Insertion Reactions of Cobalt Carbonyl

The reactions of $\text{Co}_2(\text{CO})_8$ with the carbenoids Zn, Cd, Ga^+ , InBr , TlCl , GeI_2 , SnX_2 and PbCl_2 were investigated. The compounds so prepared are listed in Table VIII, together with analytical data, melting points and colours. A detailed discussion of these reactions follows.

(i) Group II-Carbenoid Insertions:

Both metallic zinc and cadmium were found to react almost quantitatively with $\text{Co}_2(\text{CO})_8$ in THF solution, after stirring together at room temperature for an hour, affording $\text{M}[\text{Co}(\text{CO})_4]_2 \cdot 2 \text{ THF}$.



$$\text{M} = \text{Zn and Cd}$$

The zinc derivative formed very air sensitive dirty-white crystals which were soluble in n-pentane. Owing to the ease with which it decomposed, particularly in solution, it was not possible to obtain a pure product. This, together with its air sensitivity, prevented the determination of meaningful analytical data. Its mass spectrum possessed a fragment at $m/e = 406$ corresponding to $\text{Zn}[\text{Co}(\text{CO})_4]_2^+$, but none due to the THF adduct, however strong peaks $m/e = 71$ and 72 were observed which could correspond to $\text{C}_4\text{H}_7\text{O}^+$ and $\text{C}_4\text{H}_8\text{O}^+$ respectively. This compound was assumed to possess two THF molecules per molecule of compound by analogy with the well characterised cadmium compound. The zinc derivative was allowed to stand in vacuo for a week, and was

TABLE VIII

Analytical Data, Colours and Melting Points of Compounds Prepared by Insertion Reactions

Compound	M.p. °C	Colour	Calculated %				Found %			
			C	H	O	X	C	H	O	X
Cd[Co(CO) ₄] ₂ ·2 THF	-	Yellow	32.1	2.5	-	-	29.1	2.7	-	-
Cl ₂ GaCo(CO) ₄ ·THF	56-60	White	25.1	2.1	20.9	18.5	24.7	2.1	20.1	19.0
Br ₂ GaCo(CO) ₄ ·THF	82-87	Pale Yellow	20.3	1.7	16.9	33.8	19.3	1.8	15.1	34.3
BrIn[Co(CO) ₄] ₂ ·THF	72-75	Yellow	23.7	1.3	-	13.1	23.4	1.1	-	13.9
Br ₃ In ₃ Co ₄ (CO) ₁₆	dec 150	Orange	15.3	0.0	20.2	18.9	15.4	0.3	19.9	19.2
Tl[Co(CO) ₄] ₃	61-65	Dark Red	20.1	0.0	26.8	-	20.4	0.2	25.2	-
I ₂ Ge[Co(CO) ₄] ₂	dec 95	Red	14.4	0.0	-	38.0	14.2	0.0	-	38.0
Cl ₂ Sn[Co(CO) ₄] ₂	dec 106	Orange	18.1	0.0	-	13.3	19.2	0.5	-	13.3
Br ₂ Sn[Co(CO) ₄] ₂	dec 75	Orange	15.4	0.0	-	25.3	15.4	0.4	-	26.5
I ₂ Sn[Co(CO) ₄] ₂	dec 70	Purple	13.5	0.0	-	35.5	14.6	0.3	-	32.6
(AcO) ₂ Sn[Co(CO) ₄] ₂ ^b	dec 90	Orange	24.4	1.0	33.2	-	24.7	1.4	32.6	-
AcOSn[Co(CO) ₄] ₃ ^b	dec 87	Dark Red	24.4	0.4	32.4	-	24.2	0.8	31.0	-
FSn[Co(CO) ₄] ₃	84-87	Dark Red	22.1	0.0	29.5	2.9	21.9	0.1	29.8	3.8
Cl ₂ Sn[Co(CO) ₃ PPh ₃] ₂	dec 220	Orange	50.9	3.0	-	7.2	49.0	3.0	-	7.9

TABLE VIII (continued)

Compound	M.p. °C	Colour	Calculated %				Found %			
			C	H	O	X	C	H	O	X
I ₂ Ge[NiCOCP] ₂	-	Dark Red	22.9	1.6	-	-	22.4	2.0	-	-
Cl ₂ Sn[NiCOCP] ₂	dec 90	Dark Green	29.2	2.0	-	14.4	29.2	2.0	-	14.3
INiCOCP	-	Dark Green	25.8	1.8	-	-	25.0	2.0	-	-
Br ₂ GaMn(CO) ₅	dec 97	White	14.2	0.0	18.9	37.7	14.4	0.6	19.7	37.9
Br ₂ InMn(CO) ₅ ^c	dec 95	White	12.8	0.0	17.1	34.0	12.7	0.0	17.2	34.3
BrIn[Mn(CO) ₅] ₂	dec 240	Yellow	20.6	0.0	27.4	13.6	21.0	0.5	25.6	13.8
(acac)In[Mn(CO) ₅] ₂	50-52	Yellow	29.9	1.2	31.9	-	30.3	1.6	29.3	-
I ₂ InFe(CO) ₂ Cp·THF	dec 85	Yellow	22.0	2.2	5.3	42.1	20.7	2.0	7.2	40.8
I ₂ InFe(CO) ₂ Cp ^d	dec 200	Orange	15.4	0.9	5.9	46.4	15.6	0.9	6.0	47.4
I ₂ InMo(CO) ₃ Cp·THF ^e	dec 120	Yellow	21.0	1.9	9.3	36.9	21.3	1.8	8.8	38.0

^a In: Calculated, 27.2; Found, 27.0 Co: Calculated, 18.6; Found, 18.6.^b $AcO = CH_3CO_2-$ ^c In: Calculated, 24.4; Found, 24.1.^d In: Calculated, 21.0; Found, 21.0. Fe: Calculated, 10.2; Found, 10.1.^e In: Calculated, 16.7; Found, 20.2.

found to lose THF to give pale yellow crystals of the previously known compound $\text{Zn}[\text{Co}(\text{CO})_4]_2$ (9). Owing to the volatility of the latter compound, it was not possible to determine the percentage of THF by weight loss in vacuo.

The cadmium derivative formed yellow air-sensitive crystals which could be purified sufficiently for an elemental analysis by recrystallization from n-pentane. The analytical results were low in carbon, presumably due to the loss of THF, however the percentage loss in weight of a freshly purified sample, over a period of 40 hours, corresponded to loss of two moles of THF per mole of compound. The mass spectrum possessed a fragment at $m/e = 456$ corresponding to $\text{Cd}[\text{Co}(\text{CO})_4]_2^+$, but none due to the THF adduct. This is not surprising considering the high vacuum and moderately high temperatures (50°) employed in the mass spectrometer, and the ease with which the compound loses THF in vacuo.

(ii) Group III Carbenoid Insertions:

As examples of group III carbenoids, the halides of monovalent indium and thallium were investigated. Gallium, however, does not form simple well defined monovalent derivatives, so the gallium dihalides were employed. These compounds have been shown to contain both Ga(I) and Ga(III) and are formulated as $\text{Ga}^+[\text{GaX}_4]^-$ (125).

Solutions of gallium dihalides in THF were found to react with $\text{Co}_2(\text{CO})_8$ at room temperature with the formation

of $X_2GaCo(CO)_4 \cdot THF$:



X = Cl, Br and I

These compounds formed white to pale yellow, very air-sensitive, n-pentane-soluble crystals which were characterised by elemental analysis.

The exact course of this reaction is somewhat obscure owing to the lack of information concerning the species present in THF solutions of the dihalides. However, complexes such as $[Ga(dioxane)_2]Cl$ have been prepared from benzene solutions of gallium dichloride (126), which might suggest that species such as $(THF)_3GaCl$ or $[(THF)_4Ga]Cl$, together with $THF \cdot GaCl_3$ are present in THF solutions. The initial reaction with $Co_2(CO)_8$ could then be written as follows:



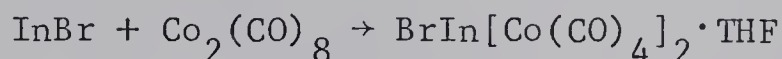
followed by a redistribution reaction:



These compounds were also prepared by anion displacement reactions as described in Chapter III.

The reaction of indium (I) bromide with $Co_2(CO)_8$ was investigated. Although this carbenoid was very soluble in THF, stirring a solution of $Co_2(CO)_8$ in this solvent with finely

powdered InBr resulted in rapid dissolution, the reaction being complete in 15 minutes. From the yellow solution produced in this reaction, yellow needle-like crystals of $\text{BrIn}[\text{Co}(\text{CO})_4]_2 \cdot \text{THF}$ were isolated:



The product was purified by recrystallization from n-pentane, and was shown by analysis and infrared spectrum to be identical to the compound prepared by an anion displacement reaction described in Chapter III.

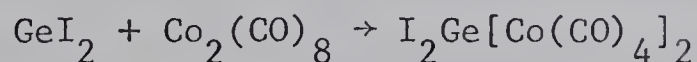
When the reaction of InBr with $\text{Co}_2(\text{CO})_8$ was carried out in benzene solution, a different product was obtained. Finely divided InBr dissolved in a benzene solution of cobalt carbonyl over a period of 12 hours affording an orange solution. Concentration of solvent gave small orange crystals insoluble in pentane, but sufficiently soluble in benzene to be recrystallized from this solvent. A complete elemental analysis of this compound agreed very closely with $\text{Br}_3\text{In}_3\text{Co}_4(\text{CO})_{16}$. Its infrared spectrum in the carbonyl stretching region (Figure 39, Chapter V) showed only terminal CO groups, the positions and intensity pattern being unlike those of any simple tetracarbonylcobalt derivatives previously investigated. There is insufficient evidence available at present to speculate on its structure, however, an X-ray structural determination is at present being carried out by Mr. P. Cradwick at this University.

In contrast to gallium and indium, it was found that thallium (I) halides did not react at all with $\text{Co}_2(\text{CO})_8$ in

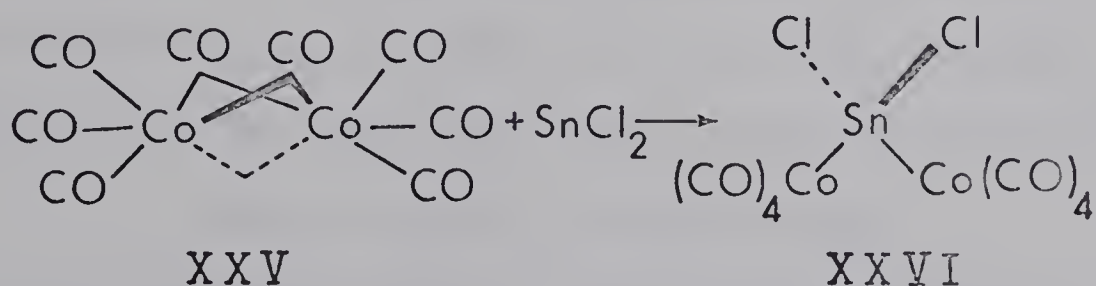
THF solution. However, thallium (I) acetylacetonate did react, but instead of the expected $(\text{acac})\text{Tl}[\text{Co}(\text{CO})_4]_2$, only $\text{Tl}[\text{Co}(\text{CO})_4]_3$ could be isolated. This compound, first reported by Hieber and Teller (9), was also prepared by an anion displacement reaction as described in chapter III.

(iii) Group IV Carbenoid Insertions:

Treatment of cobalt carbonyl with germanium diiodide afforded a dark red crystalline material characterised by elemental analysis as $\text{I}_2\text{Ge}[\text{Co}(\text{CO})_4]_2$:



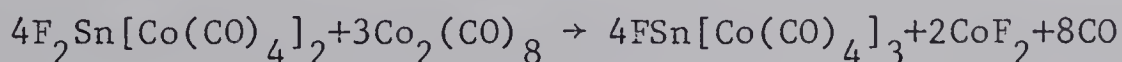
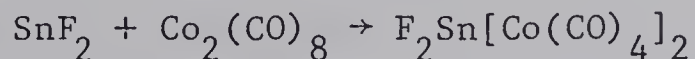
Similar reactions of tin (II) compounds produced the analogous tin (IV) derivatives $\text{X}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$. Thus treatment of a THF solution of $\text{Co}_2(\text{CO})_8$ (XXV) with equimolar amounts of SnCl_2 at room temperature afforded $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$ (XXVI):



Similar reactions occurred with SnBr_2 and SnI_2 giving the analogous bromo and iodo derivatives. These reactions proceeded rapidly, and were essentially complete after about 10 minutes at room temperature, as shown by the absence of bands due to $\text{Co}_2(\text{CO})_8$ in the infrared spectrum. The yields of these reactions

were moderately low (40-50%). Dark-red insoluble material was left behind after isolation of $X_2Sn[Co(CO)_4]_2$ indicating that other reactions besides insertion of SnX_2 were occurring. The tin compounds formed orange to purple crystals which were only moderately air sensitive, and were not noticeably changed by several days exposure to air. The above findings were later confirmed by Bonati et al. (87) who also investigated the reaction of SnX_2 with $Co_2(CO)_8$.

Attempts to prepare $F_2Sn[Co(CO)_4]_2$ by reaction of finely powdered SnF_2 with $Co_2(CO)_8$ in THF were not successful, good yields of $FSn[Co(CO)_4]_3$ only being obtained instead. The reason for this is probably the very low solubility of SnF_2 in THF. The initial step in the reaction is presumed to involve insertion of SnF_2 giving $F_2Sn[Co(CO)_4]_2$, however owing to the low solubility of SnF_2 this would occur very slowly. The initial product could then react with excess $Co_2(CO)_8$ giving the observed product $FSn[Co(CO)_4]_3$, providing the rate of this reaction is much faster than the rate of the initial insertion reaction:



This compound is pentane soluble, and is very similar to the other $XSn[Co(CO)_4]_3$ derivatives reported in Chapter II.

Reaction of tin (II) acetate with cobalt carbonyl in THF solution afforded both $(CH_3CO_2)_2Sn[Co(CO)_4]_2$ and $CH_3CO_2Sn[Co(CO)_4]_3$ in low yields. In this reaction, the rate of the initial reaction is comparable to that of the reaction of $Co_2(CO)_8$ with the

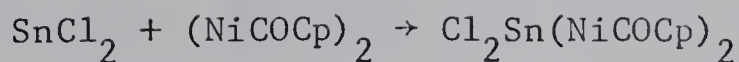
insertion product, hence both products are isolated. The molecular weight of $(\text{CH}_3\text{CO}_2)_2\text{Sn}[\text{Co}(\text{CO})_4]_2$ was found to be 765 ± 50 and was essentially the same over a concentration range of 8-23 g/l; however, the calculated value was only 578.2. This indicates that a certain amount of association is taking place, presumably via bridging acetate groups.

In contrast to GeX_2 and SnX_2 , lead carbenoids do not appear to be at all reactive towards $\text{Co}_2(\text{CO})_8$. Attempts to react PbCl_2 with cobalt carbonyl were completely unsuccessful, only starting materials being recovered.

2. Insertion Reactions of Other Dinuclear Transition Metal Complexes

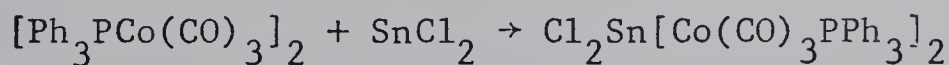
The dinuclear transition metal complexes which so far have been reported to undergo insertion reactions are $(\text{CO})_4\text{CoFe}(\text{CO})_2\text{Cp}$ (97), $\text{Co}_2(\text{CO})_8$ (89, and the present work) and $[\text{Fe}(\text{CO})_2\text{Cp}]_2$ (19), all of which possess metal-metal bonds supported by bridging carbonyl groups. It was felt that other dinuclear complexes which possess similar structures might react in an analogous way with carbenoids. This prompted the investigation of $(\text{NiCOCP})_2$, which is believed to possess a similar carbonyl bridged structure, although the CO groups are thought to be asymmetrically placed with respect to the two nickel atoms (49). Treatment of this complex in refluxing THF with SnCl_2 did indeed lead to the expected reaction $\text{Cl}_2\text{Sn}(\text{NiCOCP})_2$

being isolated:



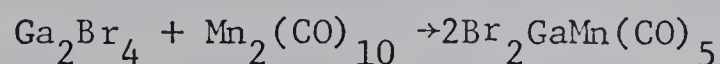
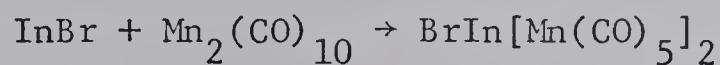
It formed dark green air sensitive crystals which were characterised by analysis. A similar reaction of GeI_2 , this time at room temperature, gave low yields of $\text{I}_2\text{Ge}(\text{NiCOCP})_2$, together with INiCOCP . The two products were characterised by analysis and by their mass spectra in which appeared fragments due to the parent ions minus one CO. The infrared spectra of both were in agreement with the expected number of carbonyl stretching bands for $\text{I}_2\text{Ge}(\text{NiCOCP})_2$ and INiCOCP , (two and one respectively). The compound INiCOCP was originally prepared by Fisher and Palm (127). The only other main group derivative of nickel so far reported is $\text{Cl}_3\text{SnNi}(\text{PPh}_3)\text{Cp}$ prepared very recently by Van Den Akker and Jellinek (128) by reaction of SnCl_2 with $\text{ClNi}(\text{PPh}_3)\text{Cp}$.

The phosphine substituted cobalt carbonyl $[\text{PPh}_3\text{Co}(\text{CO})_3]_2$ was also found to react with SnCl_2 , although under more vigorous conditions than $\text{Co}_2(\text{CO})_8$ itself. Thus reaction in refluxing THF afforded $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_3\text{PPh}_3]_2$, a compound identical to that prepared by reaction of PPh_3 with $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$.



In contrast to the dinuclear carbonyls discussed above, manganese carbonyl, $\text{Mn}_2(\text{CO})_{10}$, does not react with SnCl_2 , even when the two are refluxed in THF for several weeks (14). However it was recently discovered (129) that by using more vigorous conditions (200° in a sealed tube) SnCl_2 could be made to react with $\text{Mn}_2(\text{CO})_{10}$ to give $\text{Cl}_2\text{Sn}[\text{Mn}(\text{CO})_5]_2$. This was extended to group

III in the present work. Thus both InBr and Ga_2Br_4 were found to react with manganese carbonyl when heated to about 180° in sealed tubes for 20 hours:



The indium derivative, $\text{BrIn}[\text{Mn}(\text{CO})_5]_2$, was a bright yellow powder insoluble in non-donor solvents, but soluble in solvents such as ethyl acetate and THF. It was characterised by analysis. This compound did not form an adduct with THF, in contrast to the corresponding cobalt derivatives $\text{BrIn}[\text{Co}(\text{CO})_4]_2 \cdot \text{THF}$ indicating the stronger Lewis acidity of indium in the latter compound. The bromo derivative, $\text{BrIn}[\text{Mn}(\text{CO})_5]_2$, was converted into the corresponding acetylacetonate, $(\text{acac})\text{In}[\text{Mn}(\text{CO})_5]_2$, by treatment with thallium (I) acetylacetonate. The gallium derivative, $\text{Br}_2\text{GaMn}(\text{CO})_5$, formed pale yellow, somewhat air-sensitive crystals, soluble in CH_2Cl_2 , but not in pentane.

B. Insertion Reactions of Transition Metal Halide Complexes

INTRODUCTION

The reactions described above involved the insertion reactions of carbenoids with transition metal-metal bonds. There are also numerous reactions known which involve insertion of SnX_2 into transition metal-halogen bonds with the formation of a tin-transition metal bond.

Bonati and Wilkinson (19) reported the preparation of

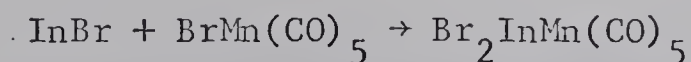
$\text{Cl}_3\text{SnFe}(\text{CO})_2\text{Cp}$ by reaction of SnCl_2 with $\text{ClFe}(\text{CO})_2\text{Cp}$, and Manning (130) later reported a similar reaction involving SnCl_2 and $\text{IFe}(\text{CO})_2\text{Cp}$ which gave $\text{ICl}_2\text{SnFe}(\text{CO})_2\text{Cp}$. In both cases insertion of tin into the Fe-Cl bond had occurred. Similar reactions have been reported for platinum halides thus treatment of $(\text{Ph}_3\text{PMe})_2(\text{PtCl}_4)$ with SnCl_2 gave $(\text{Ph}_3\text{PMe})_2[(\text{Cl}_3\text{Sn})_3\text{PtCl}_3]$ (48), while $(\text{PPh}_3)_2\text{PtCl}_2$ reacted with SnCl_2 affording $\text{Cl}_3\text{SnPt}(\text{Cl})(\text{PPh}_3)_2$ (48). In 1964 Bonati and Ugo (131) reported the preparation of $\text{Br}_3\text{SnMn}(\text{CO})_3(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$ by a similar insertion reaction involving SnBr_2 and $\text{BrMn}(\text{CO})_3(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$. More recently Taylor et al. (132) investigated the reaction of stannous chloride with such iridium complexes as $\text{H}_2\text{ClIr}(\text{PPh}_3)_3$ and $\text{HCl}_2(\text{CO})\text{Ir}(\text{PPh}_3)_2$ and were able to isolate $\text{Cl}_3\text{SnIrH}_2(\text{PPh}_3)_3$ and $\text{Cl}_3\text{SnIrHCl}(\text{CO})(\text{PPh}_3)_2$ respectively.

Insertion of SnX_2 into metal-halogen bonds thus appears to be a quite general method for synthesising trihalotin derivatives of transition metals. It was therefore decided to try extending reactions of this type to group III carbenoids in an attempt to prepare indium derivatives of such transition metals as Mn, Mo and Fe. There appear to be no previous reports of such compounds.

RESULTS AND DISCUSSION

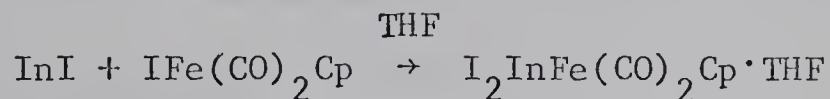
Stirring finely divided InBr with a THF solution of $\text{BrMn}(\text{CO})_5$ resulted in complete dissolution over a period of 12 hours. A white crystalline product, soluble in methylene

chloride but only slightly so in n-pentane, was isolated. This was characterised as $\text{Br}_2\text{InMn}(\text{CO})_5$ by elemental analysis:



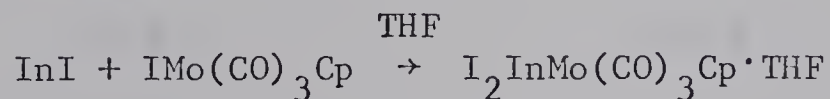
In view of the success of this reaction, it is somewhat surprising that Bonati and Wilkinson (19) were unable to find evidence of reaction of SnCl_2 with $\text{ClMn}(\text{CO})_5$.

From the reaction of InI with $\text{IFe}(\text{CO})_2\text{Cp}$ in THF, a good yield of yellow-orange crystals of $\text{I}_2\text{InFe}(\text{CO})_2\text{Cp} \cdot \text{THF}$ was obtained:



This was characterised by analysis, and the presence of one mole of THF per mole of compound confirmed by measuring the loss in weight when the product was allowed to stand at room temperature in vacuo for 26 hours. The THF adduct was soluble in CH_2Cl_2 from which it was recrystallized. However, continued recrystallization resulted in gradual loss of THF, unless 5-10% of THF had been added to the solvent. The product obtained from the THF adduct under vacuum formed very small orange crystals which were slightly soluble in CH_2Cl_2 .

A similar reaction of InI with $\text{IMo}(\text{CO})_3\text{Cp}$ afforded yellow crystals of $\text{I}_2\text{InMo}(\text{CO})_3\text{Cp} \cdot \text{THF}$:



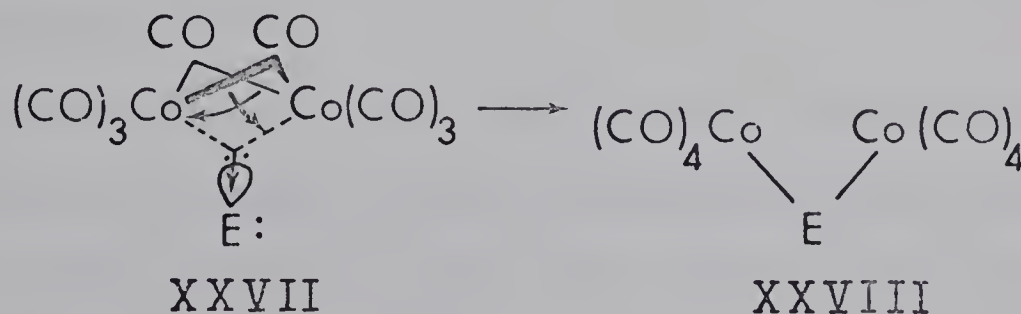
Attempts to remove THF in vacuo were unsuccessful, no loss in weight being observed after a week under vacuum. Again the analogous reaction of SnCl_2 with $\text{IMo}(\text{CO})_3\text{Cp}$ does not occur, according to a report by Manning (130) who refluxed the two

compounds together in methanol for two days.

C. Insertion Reaction Mechanisms

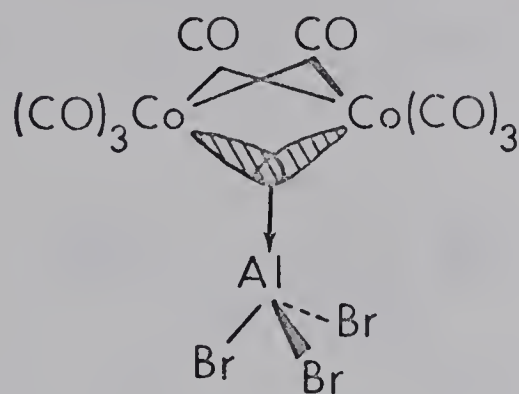
At present, no detailed quantitative studies of carbenoid insertion reactions have been carried out, so it is not possible to arrive at any definite conclusions regarding the mechanisms of these reactions. However, it is felt that a discussion of some of the possible mechanism is in order at this stage.

Direct Insertion: This mechanism involves direct attack of the carbenoid on the transition metal-metal bond and is considered to involve an intermediate in which the electrons of the bent metal-metal bond donate into an empty carbenoid orbital. In the case of cobalt carbonyl, an intermediate such as XXVII might be formed. Electron shifts and rearrangement of bridging CO groups to terminal groups would then give the observed structure XXVIII.



The formation of such an intermediate adduct seems reasonable in view of the isolation (98) of a stable adduct of $\text{Co}_2(\text{CO})_8$ with AlBr_3 shown in XXIX. This structure was supported by

its infrared spectrum which was very similar to that of $\text{Co}_2(\text{CO})_8$ itself (133).



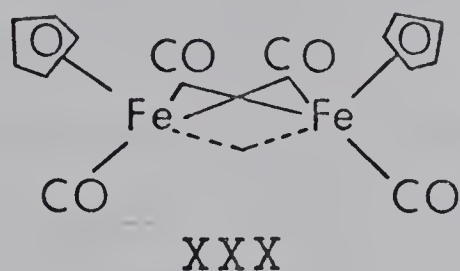
XXIX

That carbenoids can in fact act as electron acceptors was shown by King (134) who isolated a stable PPh_3 adduct of GeI_2 .

The discussion of reaction mechanism in the case of cobalt carbonyl is complicated by spectroscopic studies which show a bridged and non-bridged form of $\text{Co}_2(\text{CO})_8$ in equilibrium with each other in solution (135). It is therefore not certain that it is the bridged form which is the reactive species.

As mentioned earlier, the dinuclear transition metal complexes which possess carbonyl-bridged metal-metal bonds (e.g. $\text{Co}_2(\text{CO})_8$) appear to react with carbenoids much more readily than those having no bridging carbonyl groups. This is consistent with the mechanism under discussion, as only when the metal-metal bond is bridged with CO groups, can a suitable geometry be forced upon the molecule which allows the bond to become 'bent'; a nonbridged bond would

presumably be straight. Such a bent bond is present in the case of $\text{Co}_2(\text{CO})_8$, while solutions $[\text{Fe}(\text{CO})_2\text{Cp}]_2$ are now believed to contain a non-centrosymmetric species (XXX) with a bent metal-metal bond, on the basis of recent infrared studies (136).

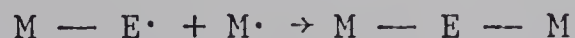
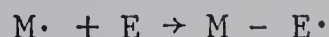


However, no structural studies have been reported for the nickel dimer $(\text{NiCOCP})_2$, aside from the suggestion based on the infrared spectrum that the CO groups are placed asymmetrically with regard to the nickel atoms (49). The presence of a bent metal-metal bond is therefore a matter of conjecture.

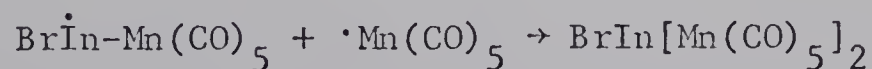
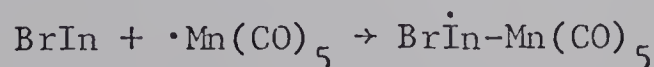
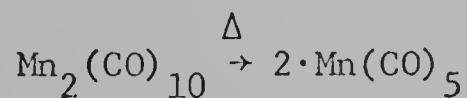
Insertion by Attack on a Transition Metal Centre: This mechanism would involve initial coordination of the carbenoid to one transition metal, followed by intramolecular migration of the other transition metal group onto the main group metal atom. Such a mechanism would resemble that postulated by Manning (130) to explain the insertion of SnCl_2 into the Fe-I bond of $\text{IFe}(\text{CO})_2\text{Cp}$, with the formation of $\text{ICl}_2\text{SnFe}(\text{CO})_2\text{Cp}$. The formation of the mixed halide was taken as evidence that the reaction does not proceed via displacement of I^- by SnCl_3^- , as such a mechanism would give rise to the trichlorotin derivative. The fact that the iodine remained associated

with the molecule suggested that the SnCl_2 molecule first coordinated to the iron atom, and was followed by migration of iodine to tin. Manning was unable to find any evidence of reaction between SnCl_2 and $\text{IMo(CO)}_3\text{Cp}$. This he explained on the basis of the seven-coordinate intermediate $\text{CpFe(CO)}_2(\text{SnCl}_2)\text{I}$ being more readily formed than the eight-coordinate $\text{CpMo(CO)}_3(\text{SnCl}_2)\text{I}$. It is pertinent to note that in the present work InI was found to react with $\text{IFe(CO)}_2\text{Cp}$ over a period of 1.5 hours, whereas with $\text{IMo(CO)}_3\text{Cp}$ the reaction took 12 hours to reach completion. Possibly these reactions proceed via a similar mechanism.

Dissociative Insertion: A third possibility for a reaction mechanism would involve the initial homolytic fission of the metal-metal bond, followed by attack of the carbenoid by the fragments:



It is conceivable that such a mechanism operates in the reaction of $\text{Mn}_2(\text{CO})_{10}$ with InBr , for example, where much higher temperatures (180-200°) are required:



Such a mechanism is supported by recent rate studies of the reaction of $\text{Mn}_2(\text{CO})_{10}$ with PPh_3 (137) which suggested that

homolytic cleavage of the Mn-Mn bond was occurring. The reactions were carried out in such solvents as xylene and decalin, and it was suggested that pairs of $\cdot\text{Mn}(\text{CO})_5$ radicals were trapped in solvent cages. The authors felt that such Mn-Mn bond cleavage was energetically feasible considering the value of 19 kcal./mole recently determined by mass spectroscopic studies (138) for the Mn-Mn bond dissociation energy. In the present case the radical pairs could be trapped in $\text{Mn}_2(\text{CO})_{10}$ cages, the solvent being the molten carbonyl itself.

EXPERIMENTAL

Reagents and general procedures are the same as described in Chapter II.

Starting Materials

Gallium dichloride, Ga_2Cl_4 : A modification of the procedure of Carlston et al. (139) was employed. Metallic gallium (6.987 g., 100 mmole.) was placed at the bottom of a 1.5 cm. x 30 cm. glass tube and melted by heating to 70°. Mercuric chloride (27.15 g. 100 mmole.) was then added after flushing the tube with nitrogen. The addition was carried out cautiously in 1 g. portions as much heat is initially evolved. When all of the HgCl_2 had been added, the tube was heated to 130° for two hours. The tube was then cooled and the solid product removed and separated from the Hg which had settled to the bottom. The product was stored under nitrogen and used without further purification.

Gallium dibromide, Ga_2Br_4 : This was prepared in a similar way to Ga_2Cl_4 as described above. The reaction was not nearly as violent, however, and the gallium was heated to 110° before HgBr_2 addition. When addition was complete the tube was heated to 160-180° for two hours to complete the reaction. Gallium Diiodide was prepared in the same way.

Indium(I) bromide, InBr : This was prepared by Klemm and Dierks procedure (140). Indium tribromide (108 g.

305 mmole.) was mixed with excess indium metal (75 g.) and heated under nitrogen to melt the InBr_3 . The indium metal dissolves vigorously giving a red melt. When no more metal would dissolve, the resultant crude InBr was distilled under a high vacuum giving pure product.

Indium(I) iodide, InI : A mixture of 22.95 g. (200 mmole.) of indium metal and 45.45 g. (100 mmole.) of HgI_2 were cautiously heated together in a vessel fitted with an air reflux condenser. When the initial vigorous reaction had subsided, the melt was heated more strongly for 15 minutes so that the mercury produced in the reaction was refluxing. The very dark red melt was then cooled and the solid separated from the bulk of the mercury. The solid was then pulverised and heated to distill off any remaining mercury. The resultant dark crimson solid was used without further treatment.

Germanium diiodide, GeI_2 : This was made by the procedure of Brauer (141). Germanium tetraiodide (20 g.) was refluxed with a mixture of 10 ml. of 57% HI and 20 ml. of water to which 7.6 ml. of 50% hypophosphorous acid was added. The reaction was complete when the red crystals of GeI_4 had been converted to yellow GeI_2 . The mixture was then cooled to 0° and the crystals of product filtered off and washed with dilute HI . The material was vacuum dried at 110° over P_2O_5 to sublime off unreacted GeI_4 . The product was used

without further purification.

Bis(triphenylphosphine)hexacarbonyldicobalt(0),

$[\text{Ph}_3\text{PCo}(\text{CO})_3]_2$: Using the procedure described by Hieber and Breu (142), $\text{Co}_4(\text{CO})_{12}$ (2.0 g., 3.5 mmole.) was dissolved in 50 ml. of p-xylene, and 4.0 g. (15.3 mmole.) of PPH_3 added. The mixture was heated to 35° and stirred for 1.5 hours. The dark brown precipitate which was formed was filtered off, washed with acetone, and dried in vacuo at room temperature affording a yield of 3.6 g.

Bis(π -cyclopentadienyl)dicarbonyldinickel(0),

$[\text{CpNiCO}]_2$: The procedure described by King (143) was used to prepare this compound. A mixture of 31.2 g. (165 mmole.) of nickelocene, 60 ml. (75 g., 465 mmole.) of $\text{Ni}(\text{CO})_4$ and 200 ml. of benzene was refluxed gently for at least five hours in an efficient fume hood because of the extreme toxicity of $\text{Ni}(\text{CO})_4$. The green colour of nickelocene soon changed to the blood red colour of the product. At the end of the reaction period, the mixture was cooled, and excess benzene and $\text{Ni}(\text{CO})_4$ removed under reduced pressure via a -78° trap to condense most of the excess $\text{Ni}(\text{CO})_4$. The residue was extracted with 450 ml. of anhydrous ether in four portions. The extracts were then passed through a 2 x 15 cm. alumina filled column to remove $\text{Cp}_3\text{Ni}_3(\text{CO})_2$, a by-product of the reaction. The column was washed with ether to remove dimer, and the solvent removed from the combined eluates to give crystals of product which were

pure enough to use without further treatment.

Iodo(π -cyclopentadienyl)tricarbonylmolybdenum(-I),

IMo(CO)₃Cp: This was made by the method of Abel et al. (144).

A solution of 4.90 g. (10 mmole.) of [CpMo(CO)₃]₂ in 200 ml. of chloroform was slowly added to a stirred room temperature solution of 2.60 g. (10.2 mmole.) of I₂ in the same solvent. When the addition was complete, the solution was washed with aqueous Na₂S₂O₃ solution to remove excess I₂, and then dried with anhydrous Na₂SO₄. After filtration, the solution was evaporated to dryness and the residue recrystallized by evaporation of an n-pentane/CH₂Cl₂ solution affording 4.6 g. of pure product.

Preparation of Tetracarbonylcobalt Derivatives

Bis(tetracarbonylcobalt)zinc(II) Tetrahydrofuranate,

Zn[Co(CO)₄]₂.THF: A solution of 3.4 g. (10 mmole.) of Co₂(CO)₈ in 40 ml. of THF was stirred at room temperature for about one hour with excess zinc powder (about 5 g.). At the end of this time the original dark red solution had become pale yellow. THF was removed from the mixture by evaporation under reduced pressure, and the residue extracted with 50 ml. of dry, oxygen free n-pentane. The extract was centrifuged and cooled to -80° affording 5.6 g. of white crystals of crude product contaminated by dark material. It was recrystallized twice by dissolving in 100 ml. of n-pentane and recooling to -80° giving 3.5 g. of dirty-white needle-like crystals. It was not possible to obtain

absolutely pure material owing to the rapidity with which it reacts with air, and the ease with which it decomposes in solution.

Bis(tetracarbonylcobalt)cadmium(II) tetrahydrofuranate, $\text{Cd}[\text{Co}(\text{CO})_4]_2 \cdot \text{THF}$: Cadmium metal (4.0 g.) in small pieces was stirred with a solution of 3.4 g. (10 mmole.) of $\text{Co}_2(\text{CO})_8$ in 50 ml. of THF for 50 minutes. At the end of this period the solution had become yellow, and was decanted from excess metal and evaporated to dryness. The residue was extracted with 50 ml. of n-pentane, and the extract centrifuged, evaporated to 10 ml. and cooled to -80° . This produced 5.3 g. of yellow crystals of product which were recrystallized from 15 ml. of n-pentane(+ 5% THF) by cooling to -20° . This afforded 4.0 g. of pure product.

Dichloro(tetracarbonylcobalt)gallium(III) tetrahydrofuranate, $\text{Cl}_2\text{GaCo}(\text{CO})_4 \cdot \text{THF}$: Gallium dichloride (7.2 g., 25.6 mmole.) was added to 50 ml. of THF at -80° , and the mixture allowed to warm up slowly with constant stirring. To this Ga_2Cl_4 solution, 8.5 g. (25.0 mmole.) of $\text{Co}_2(\text{CO})_8$ in 50 ml. of THF was added and the mixture stirred at room temperature for 30 minutes. After removal of THF at reduced pressure, the residue was extracted first with 25 ml. of n-pentane to remove excess $\text{Co}_2(\text{CO})_8$, and then with 600 ml. of the same solvent to extract product. This extract was concentrated to about 50 ml., and cooled to -80° affording

6.6 g. of white needles of product which were recrystallized from n-pentane at -80° . Owing to the ease with which the product undergoes atmospheric oxidation great care was exercised to prevent no more than minimal contact of solid or solution with the atmosphere.

The corresponding dibromo and diiodo derivatives were prepared in the same way as above using equimolar quantities of reactants. The iodo derivative, however, was too unstable to obtain pure enough for analysis.

Bromobis(tetracarbonylcobalt)indium(III) tetrahydrofuranate, $\text{BrIn}[\text{Co}(\text{CO})_4]_2 \cdot \text{THF}$: Finely powdered InBr (9.7 g., 50 mmole.) was suspended in a well-stirred solution of 17.0 g. (49.7 mmole.) of $\text{Co}_2(\text{CO})_8$ in 100 ml. of THF at room temperature. After 15 minutes the InBr had completely dissolved giving an orange solution. The solvent was removed under reduced pressure, and the residue extracted with n-pentane. This extract was cooled to -80° whereupon orange-yellow needles of product were deposited. Recrystallization from n-pentane at -80° afforded product as yellow needles in 73% yield. Repeated recrystallization from n-pentane resulted in gradual loss of THF as indicated by analyses of products which had been repeatedly recrystallized.

Molecular weight calculated for $\text{BrIn}[\text{Co}(\text{CO})_4]_2 \cdot \text{THF}$, 608.7; found, 607 in benzene solution.

Tribromotriindiumtetracobalthexadecakiscarbonyl,

$\text{Br}_3\text{In}_3\text{Co}_4(\text{CO})_{16}$: A solution of 6.84 g. (20 mmole.) of $\text{Co}_2(\text{CO})_8$ in 100 ml. of benzene was stirred for 12 hours at room temperature with 5.84 g. (30 mmole.) of finely divided InBr. At the end of this period the InBr had completely dissolved producing an orange solution. It was filtered and evaporated to a small volume affording a 79% yield of orange crystalline product. It was purified by evaporation of a benzene solution to a small volume.

Tris(tetracarbonylcobalt)thallium(III), $\text{Tl}[\text{Co}(\text{CO})_4]_3$:

Thallium (I) acetylacetonate (1.0 g., 3.3 mmole.) in THF was added to 1.0 g. (2.8 mmole.) of $\text{Co}_2(\text{CO})_8$ in the same solvent stirred initially at -78° . On warming to 0° the solution turned deep purple and evolved CO. The solvent was removed under reduced pressure when gas evolution had ceased, and the residue extracted with n-pentane. The extract was cooled to -78° affording deep-red crystals in 10% yield after recrystallization.

Diodobis[tetracarbonylcobalt]germanium(IV), $\text{I}_2\text{Ge}[\text{Co}(\text{CO})_4]_2$:

Germanium (II) iodide (3.26 g., 10 mmole.) was added to a solution of $\text{Co}_2(\text{CO})_8$ (3.4 g., 10 mmole.) in THF which was stirred at room temperature for 10 minutes. At the end of this reaction time, the solvent was removed under reduced pressure, and the residue extracted with n-pentane. The extract, after concentrating to about 10 ml., was cooled to

0° affording red needles. After two recrystallizations from n-pentane, 2.0 g. of pure product was obtained.

Dichlorobis[tetracarbonylcobalt]tin(IV), $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$:

A solution of anhydrous stannous chloride (5.7 g., 30 mmole.) in 100 ml. of THF was added to 10.3 g. (30 mmole.) of $\text{Co}_2(\text{CO})_8$ in 150 ml. of the same solvent, and the mixture stirred at room temperature for 15 minutes. After removal of solvent under reduced pressure, the residue was dissolved in the minimum amount of methylene chloride. This deep-red solution was filtered and cooled in ice. Slow addition of n-pentane afforded orange-red crystals which were recrystallized from methylene chloride and n-pentane affording a 50% yield of product. The product could also be separated from the crude reaction mixture, after removal of THF, by extraction with a large volume of n-pentane followed by evaporation to a small volume and cooling.

Dibromobis[tetracarbonylcobalt]tin(IV), $\text{Br}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$;

and Diiodobis[tetracarbonylcobalt]tin(IV), $\text{I}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$:

These were prepared in the same way as the dichloro derivative, as described above, using 10 mmole. of SnX_2 and 10 mmole. of $\text{Co}_2(\text{CO})_8$ in THF. After allowing these to react for 10 minutes, the solvent was removed, and the residue extracted with n-pentane. Evaporation to low volume, followed by cooling to -20°, gave crystals of product.

Recrystallization from n-pentane afforded a 55% yield of $\text{Br}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$, and a 38% yield of $\text{I}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$.

Reaction of Stannous Acetate with $\text{Co}_2(\text{CO})_8$: Stannous acetate (9.0 g., 38 mmole.) was suspended in a solution of 6.6 g. (19.3 mmole.) of $\text{Co}_2(\text{CO})_8$ in 100 ml. of THF and stirred at room temperature. After 15 minutes the THF was removed at reduced pressure and the residue extracted with 500 ml. of n-pentane in small portions leaving 6.0 g. of red insoluble residue. The pentane extract was evaporated under reduced pressure to 50 ml. and cooled in a freezer to -20° . Orange crystals came down overnight, and were recrystallized twice from n-pentane at -20° affording 0.4 g. of pure $[\text{CH}_3\text{CO}_2]_2\text{Sn}[\text{Co}(\text{CO})_4]_2$. The n-pentane mother liquor from the initial extraction was evaporated to 5 ml. and cooled to -20° . This gave dark-red crystals which were recrystallized from n-pentane at -20° affording 0.4 g. of pure $\text{CH}_3\text{CO}_2\text{Sn}[\text{Co}(\text{CO})_4]_3$.

Molecular weight calculated for $[\text{CH}_3\text{CO}_2]_2\text{Sn}[\text{Co}(\text{CO})_4]_2$: 578.2. Found in cyclohexane solution: 755 ± 20 , (8.02 g./l.); 765 ± 50 , (22.9 g./l.).

Fluorotris(tetracarbonylcobalt)tin(IV), $\text{FSn}[\text{Co}(\text{CO})_4]_3$: Finely divided SnF_2 (4.0 g., 26.6 mmole.) was suspended in a solution of 7.2 g. (21.0 mmole.) of $\text{Co}_2(\text{CO})_8$ in 100 ml. of THF and stirred at room temperature for five hours. After decanting the solution from excess SnF_2 , the solvent was

removed under reduced pressure and the residue extracted with 150 ml. of n-pentane. The extract was cooled to -20° to give 4.0 g. of dark-red crystals of product. Two recrystallizations from n-pentane at -20° afforded 3.4 g. of pure product.

Dichlorobis(triphenylphosphinetricarbonylcobalt)tin(IV),

$\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_3\text{PPh}_3]_2$: (i) A suspension of 1.0 g. (1.23 mmole.) of $[\text{Co}(\text{CO})_3\text{PPh}_3]_2$ in 50 ml. of THF containing 0.24 g. (1.27 mmole.) of SnCl_2 was refluxed with stirring for three hours. At the end of this period the solvent was removed under reduced pressure and the residue extracted with dichloromethane. Slow addition of n-pentane to the extract, followed by cooling in Dry Ice, gave red crystals of product.

(ii) The same product was prepared by refluxing a solution of 0.55 g. (2.1 mmole.) of PPh_3 with 0.53 g. (1.0 mmole.) of $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$ in 50 ml. of THF. After two hours the THF was removed under reduced pressure and extracted with dichloromethane. Addition of n-pentane followed by cooling to -20° afforded a compound which was shown to be identical to the product obtained by method (i) by comparison of infrared spectra.

Preparation of Other Transition Metal Derivatives

Dichlorobis(π -cyclopentadienylcarbonylnickel)tin(IV),

$\text{Cl}_2\text{Sn}[\text{CpNiCO}]_2$: A mixture of SnCl_2 (0.8 g., 4.2 mmole.) and 1.0 g. (3.3 mmole.) of $[\text{CpNiCO}]_2$ dissolved in 50 ml. of THF

was refluxed for two hours. The solvent was removed under reduced pressure and the residue extracted with n-hexane. After filtering and cooling to -20° , very dark green needle-like crystals of product were formed. These were purified by dissolving in the minimum quantity of THF and adding n-hexane slowly with cooling to -20° .

Diodobis(π -cyclopentadienylcarbonylnickel)germanium(IV),

$\text{I}_2\text{Ge}[\text{CpCO}]_2$: A solution of 1.4 g. (4.62 mmole.) of $[\text{CpNiCO}]_2$ in 40 ml. of THF was stirred at room temperature with 1.5 g. (4.59 mmole.) of GeI_2 . After two hours the THF was removed and the residue extracted with 250 ml. of n-pentane. The extract was filtered, evaporated to 40 ml. and cooled to -20° for two hours. The dark-red material which was deposited was recrystallized three times from n-pentane affording 0.2 g. of $\text{I}_2\text{Ge}[\text{NiCOCp}]_2$. The mother liquor from the original extraction was evaporated to about 5 ml. giving 0.25 g. of dark green crystals which were purified by three recrystallizations from n-pentane affording pure INiCpCO .

Dibromo(pentacarbonylmanganese)gallium(III), $\text{Br}_2\text{GaMn}(\text{CO})_5$:

A mixture of 4.6 g. (10.0 mmole.) of Ga_2Br_4 and 3.3 g. (9.85 mmole.) of $\text{Mn}_2(\text{CO})_{10}$ was placed in a glass tube (2 cm. x 30 cm.) which was then cooled to -78° , evacuated and sealed. The tube was placed in a tube furnace and heated to 180 - 190° for 19 hours. The tube was then allowed to cool to room temperature, and then further cooled in liquid nitrogen to condense any

CO which might have formed. The tube was opened and the solid extracted first with n-pentane to remove unreacted $\text{Mn}_2(\text{CO})_{10}$, and then with dichloromethane to remove product. The latter extract was centrifuged, evaporated to a small volume, and cooled to -20° affording 2.0 g. of white crystals. These were twice recrystallized from 15 ml. of dichloromethane by n-pentane addition affording 0.4 g. of white glistening crystals of pure product.

Bromobis(pentacarbonylmanganese)indium(III), $\text{BrIn}[\text{Mn}(\text{CO})_5]_2$:

A mixture of 2.0 g. (10.2 mmole.) of InBr and 3.3 g. (8.5 mmole.) of $\text{Mn}_2(\text{CO})_{10}$ was heated to 180° in a sealed evacuated tube for 22 hours. After cooling in liquid nitrogen and opening the tube, the solid product was extracted first with dichloromethane to remove $\text{Mn}_2(\text{CO})_{10}$, and then with THF to extract product. The latter extract was filtered, evaporated to 2 ml. and n-pentane added with cooling to -20° . This gave 2.5 g. of a bright yellow solid which was recrystallized from THF and pentane affording a 40% yield of pure product.

(Acetylacetonato)bis(pentacarbonylmanganese)indium(III),

$(\text{acac})\text{In}[\text{Mn}(\text{CO})_5]_2$: Thallium (I) acetylacetonate (0.5 g., 1.65 mmole.) in THF was added to 0.9 g. (1.7 mmole.) of $\text{BrIn}[\text{Mn}(\text{CO})_5]_2$ in the same solvent stirred at room temperature. After five minutes the precipitated TlBr was removed under reduced pressure. The residue was extracted with n-pentane, the extract evaporated to about 0.5 ml., and cooled to -20°

affording yellow crystals. A yield of 0.4 g. was obtained on recrystallization from *n*-pentane.

Dibromo(pentacarbonylmanganese)indium(III), $\text{Br}_2\text{InMn}(\text{CO})_5$:

A solution of 1.4 g. (5.1 mmole.) of $\text{BrMn}(\text{CO})_5$ in 40 ml. of THF was stirred at room temperature with a suspension of 1.0 g. (5.14 mmole.) of finely divided InBr. The InBr had completely dissolved in 12 hours affording a colourless solution. The solvent was removed and the residue extracted with dichloromethane. The extract was centrifuged and evaporated to a small volume. Slow addition of *n*-pentane followed by cooling to -20° afforded white crystals of product in a yield of 0.7 g. after recrystallization from CH_2Cl_2 and *n*-pentane.

Diiodo(π -cyclopentadienyldicarbonyliron)indium(III)

tetrahydrofuranate, $\text{I}_2\text{InFe}(\text{CO})_2\text{Cp}\cdot\text{THF}$: Finely divided InI (6.0 g., 24.9 mmole.) was suspended in a stirred room temperature solution of 5.0 g. (19.7 mmole.) of $\text{IFe}(\text{CO})_2\text{Cp}$ in 70 ml. of THF. After 1.5 hours the solvent was removed under reduced pressure, the solution having turned from dark-red to yellow-brown. The residue was then extracted with 20 ml. of dichloromethane to which about 5 ml. of THF had been added. The extract was filtered and 200 ml. of *n*-pentane added rapidly with vigorous swirling causing a dark oil to settle and leaving a milky yellow-orange solution behind. When all of the oily impure material had settled, the cloudy solution was cooled to -20° affording orange-yellow crystals

of product. The oil was treated with further quantities of THF and n-pentane and the solution cooled giving a further crop of crystals. The combined products were recrystallized from dichloromethane (+ 10% THF) by n-pentane addition and cooling to -20° affording 60% of pure product.

Diiodo(π -cyclopentadienyldicarbonyliron)indium(III),

$I_2InFe(CO)_2Cp$: A 0.7038 g. sample of $I_2InFe(CO)_2Cp \cdot THF$ was subjected to a pressure of 0.05 mm of Hg for 26 hours at room temperature. At the end of this period the sample had reached constant weight. The percentage loss in weight was 12.5% (THF calculated for $I_2InFe(CO)_2Cp \cdot THF = 11.7\%$) The resultant light orange powder was recrystallized by evaporation of a saturated dichloromethane solution to a small volume.

Diiodo(π -cyclopentadienyltricarboxymolybdenum)Indium(III)

tetrahydrofuranate, $I_2InMo(CO)_3Cp \cdot THF$: A solution of 1.86 g. (5.0 mmole.) of $IMo(CO)_3Cp$ in 50 ml. of THF was stirred at room temperature with 1.5 g. (6.2 mmole.) of finely divided InI. After 12 hours the solution had become a dirty yellow colour. The solvent was removed under reduced pressure, and the residue extracted with 16 ml. of dichloromethane to which about 15 drops of THF had been added. After filtration, the extract was evaporated to about 13 ml. and 3 ml. of n-pentane added giving a dirty-yellow precipitate of impure material which was rejected. The solution was then made up to 50 ml. with

n-pentane and cooled to -20° giving 2.5 g. of crude product.

It was purified by suspending in 20 ml. of n-pentane and adding about 20 ml. of dichloromethane until all the crystals had just dissolved. This solution was centrifuged, evaporated to 5 ml., and cooled to -20° affording 1.8 g. of yellow crystals of pure product.

CHAPTER V

Spectroscopic Studies

A. Infrared Spectra in the Carbonyl Stretching Region

INTRODUCTION

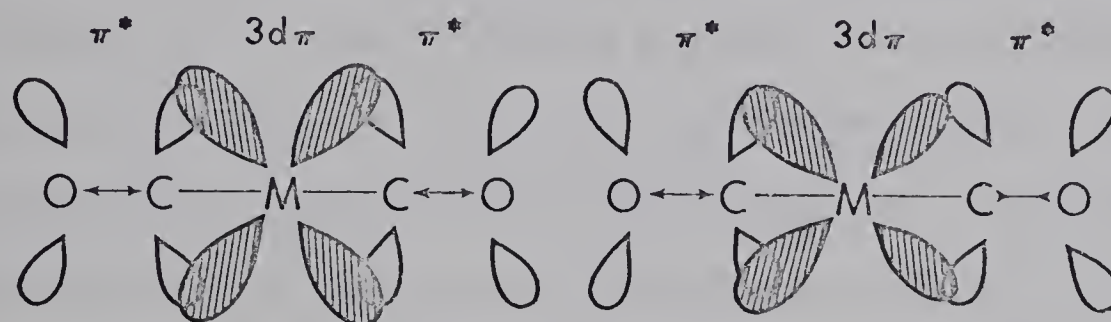
Carbonyl complexes of transition metals, such as $\text{Fe}(\text{CO})_5$, exhibit strong sharp absorption bands in the infrared in the region 2100 to 1800cm^{-1} . These bands are due to absorption of infrared radiation at frequencies corresponding to C-O stretching vibrations. The dipole moment of the carbonyl group changes as it vibrates, and it is this change in dipole moment which allows it to absorb electromagnetic radiation at a frequency equal to that at which it is vibrating, although, in reality, all of the CO groups are coupled, and it is the resultant oscillating dipole moment of the whole molecule that is responsible for absorption of radiation. Classically, the absorption can be thought of as occurring via interaction of the oscillating dipole with the electric vector of the radiation.

In discussing CO vibrational spectra, it is usually assumed that no coupling between CO vibrations and any other molecular vibrations occurs, bands due to CO vibrations being well separated from any other infrared bands.

It is generally believed that the metal-carbon bond in metal carbonyls involves initial formation of a sigma bond by

donation of the carbon lone pair into an empty metal hybrid orbital, followed by back donation of filled metal d orbitals into empty antibonding CO π^* orbitals (π^* orbitals). This M-C π bonding removes excess charge built up on the metal by the initial σ donation. The σ bonding can then proceed more extensively than would otherwise be possible, because of the formation of π bonds. Conversely, the accumulation of negative charge on the metal stimulates more extensive π donation to the CO group thus giving rise to a stronger π bond. Thus the effect of the two types of bonding together is much greater than the sum of the effects they would produce separately, and is referred to as a synergic interaction. The metal-carbon π bonding, by putting electron density into the π^* orbitals of CO, has the effect of decreasing the π bond order of the C-O bond. Thus an increase of M-C π bonding causes a decrease of C-O π bonding. This is reflected in the observed stretching frequencies of metal carbonyls for which values ranging from 2100 to 1800 cm^{-1} are usually observed, indicating a C-O bond order between two and three (carbon monoxide absorbs at 2140 cm^{-1} , whereas ketones absorb at about 1700 cm^{-1} .) Because of M-C π overlap, CO groups on one metal can all interact with each other. More specifically the vibration of one CO is coupled to the vibrations of the other CO groups. Stretching the C-O bond from its equilibrium position decreases the overlap of carbon

and oxygen 2p atomic orbitals, thus lowering the energy of the π^* molecular orbital. This will increase the overlap between the filled metal d orbitals and the CO π^* orbital. Conversely, compressing a CO group reduces metal-carbon π overlap. Thus $d_{\pi} \rightarrow \pi^*$ overlap decreases for the contracting CO and increases for the stretching CO. There is consequently less competition for the metal d-electron density when one CO contracts and the other stretches (XXXII), than when both stretch simultaneously (XXXI). In other words, stretching both CO groups at the same time is more difficult, having a greater energy requirement, than stretching one CO and compressing the other. In general

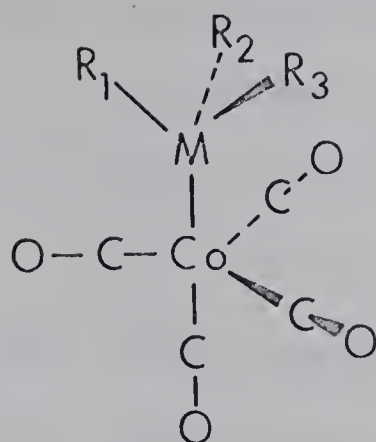


XXXI

XXXII

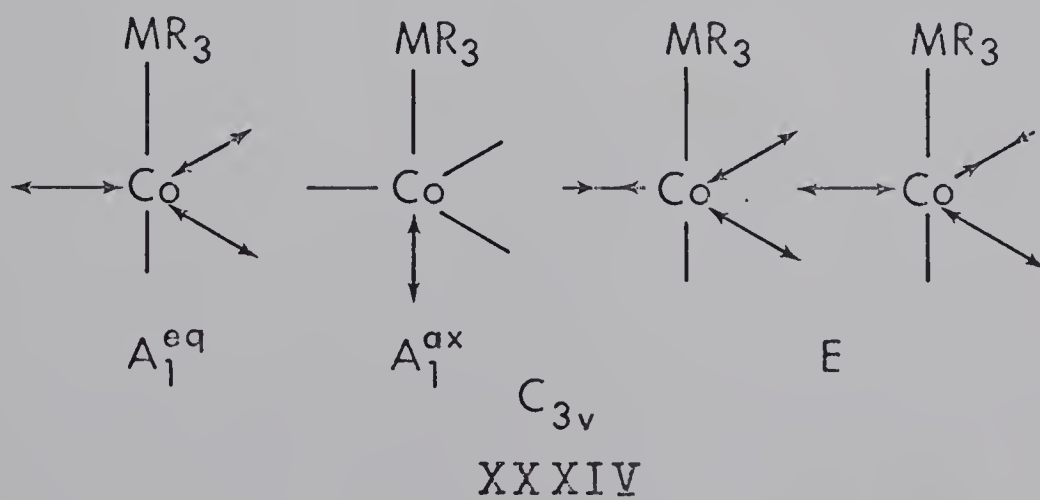
that vibration which involves the symmetric stretching of the greatest number of CO groups will have the highest frequency. This conclusion is very useful when trying to assign the observed frequencies to the various possible modes of vibration.

The condition for a molecular vibration to absorb infrared radiation is that it must be associated with a change in the dipole moment of the whole molecule. In the case of the symmetric vibration XXXI the dipole moment changes of both CO groups are equal and in opposite directions, and thus cancel. The resultant change in dipole moment is therefore zero, and will not give rise to infrared absorption (it is infrared inactive). The asymmetric vibration XXXII, however, is infrared active as both dipole changes are in the same direction and add together. It is usual to represent the change in dipole moment on vibration as a vector and is symbolized by an arrow in most of the diagrams in this chapter. If the above hypothetical $M(CO)_2$ molecule were not linear, however, both modes of vibration would become infrared active as both would possess non-zero dipole changes. In the case of molecules with three or more CO groups attached to one central metal atom, the number of infrared active vibrational modes of the molecule cannot always be easily determined by inspection. Use is then made of group theory and symmetry arguments. The actual procedure used to determine the number and symmetry of the carbonyl stretching modes is beyond the scope of the present work, and is discussed in detail in many texts on the subject (e.g. 145, 146). As an example of the results of these procedures, the compounds $R_3MCo(CO)_4$ ($R_1 = R_2 = R_3$ in XXXIII) which have C_{3v} symmetry, are predicted



C_{3v} when $R_1 = R_2 = R_3$
 C_s otherwise
 XXXIII

to have three infrared-active vibrational modes which are labelled A_1^{eq} , A_1^{ax} and E. These modes are pictured in XXXIV where the arrow heads indicate the direction of vibration of the C and O atoms, and a line without arrows represents a CO group which is



not vibrating. The two modes labelled E in XXXIV will both have exactly the same frequency, and the E mode is said to be doubly degenerate. It should be pointed out at this stage that the two A_1 modes are not considered to be accurately described by the vibrations shown in XXXIV. It is believed that a certain amount of coupling occurs between equatorial and axial stretching so that the two modes should really be represented by a certain combination of $A_1^{(2)}$ and $A_1^{(1)}$ rather than A_1^{eq} and A_1^{ax} . This coupling is discussed in more detail later.

RESULTS AND DISCUSSION

1. Infrared Spectra of Mono(tetracarbonylcobalt) Derivatives

(i) Assignment of Observed Frequencies

The observed carbonyl stretching frequencies ($\nu(\text{CO})$) are listed in Table IX, and a selection of typical spectra are reproduced in Figures 2 to 16. (Figures are collected at the end of Chapter V).

The geometry of the $\text{Co}(\text{CO})_4$ group in all of these compounds is assumed to be trigonal bipyramidal, with the main group atom in an axial position (XXXI). This assumption is supported by X-ray structural determinations of numerous tetracarbonylcobalt derivatives, such as $\text{Cl}_3\text{SiCo}(\text{CO})_4$ (68), $\text{PPh}_3\text{AuCo}(\text{CO})_4$ (61), $\text{Zn}[\text{Co}(\text{CO})_4]_2$ (65), and $\text{Hg}[\text{Co}(\text{CO})_4]_2$ (8).

The symmetry of the mono(tetracarbonylcobalt) derivatives is C_{3v} if there is a three-fold axis of rotation through the M-Co bond, such as in $\text{Me}_3\text{SnCo}(\text{CO})_4$, and C_s otherwise, such as in $\text{PhCl}_2\text{GeCo}(\text{CO})_4$. As was shown in the Introduction, three infrared active bands in the $\nu(\text{Co})$ region are predicted for C_{3v} derivatives, and in every case studied in this work three bands were in fact observed (Table IX, Figures 2 to 8). In each case two high frequency bands of medium intensity, and one low frequency band of much higher intensity were seen. The observed bands can be tentatively assigned to the three predicted modes (A_1^{eq} , A_1^{ax} , E) by consideration of the relative intensities of the bands. The intensity of an infrared band is proportional to the square of the resultant

TABLE IX

Infrared Carbonyl Stretching Frequency Data for

Mono(tetracarbonylcobalt)derivatives

Compounds with C_{3v} symmetry	$\nu(CO), cm^{-1}$ ^a		
	$\overbrace{A_1^{(2)}}^{(2)}$	$\overbrace{A_1^{(1)}}^{(1)}$	E
$Cl_3GeCo(CO)_4$	2122 (6.4)	2069 (6.5)	2050 (10)
$Br_3GeCo(CO)_4$	2118 (6.4)	2066 (5.8)	2048 (10)
$I_3GeCo(CO)_4$	2113 (7.4)	2062 (5.2)	2042 (10)
$Ph_3GeCo(CO)_4$	2091 (7.2)	2030 (7.2)	2006 (10)
$Cl_3SnCo(CO)_4$	2120 (8.0)	2068 (6.8)	2048 (10)
$Br_3SnCo(CO)_4$	2116 (8.1)	2063 (6.3)	2043 (10)
$I_3SnCo(CO)_4$	2109 (8.0)	2058 (4.6)	2037 (10)
$Ph_3SnCo(CO)_4$	2087 (6.6)	2027 (5.1)	1999 (10)
$Me_3SnCo(CO)_4$	2082 (7.3)	2020 (6.9)	1988 (10)
$Ph_3PbCo(CO)_4$	2081 (8.0)	2022 (4.9)	1997 (10)
Compounds with C_s symmetry	A' (2)	A' (1)	$\overbrace{A' + A''}^{A' + A''}$
$Cl_2GaCo(CO)_4 \cdot THF^b$	2095 (5.9)	2035 (6.4)	2012 (10) 2000 (8.9)
$Br_2GaCo(CO)_4 \cdot THF^b$	2096 (7.2)	2036 (7.5)	2012 (10) 2001 (9.3)
$Br(acac)GaCo(CO)_4$	2096 (5.2)	2035 (7.7)	2013 (10) 2001 (8.7)
$Cl_2PhGeCo(CO)_4$	2112 (7.8)	2056 (8.3)	2038 (9.7) 2027 (10)
$I_2PhGeCo(CO)_4$	2106 (8.5)	2052 (6.7)	2033 (9.4) 2024 (10)
$I_2MeGeCo(CO)_4$	2106 (8.7)	2053 (8.2)	2033 (9.8) 2022 (10)
$ClPh_2GeCo(CO)_4$	2101 (7.6)	2043 (7.9)	2026 (10) 2010 (10)
$ClMe_2GeCo(CO)_4$	2100 (7.4)	2041 (8.3)	2021 (9.9) 2004 (10)

TABLE IX (continued)

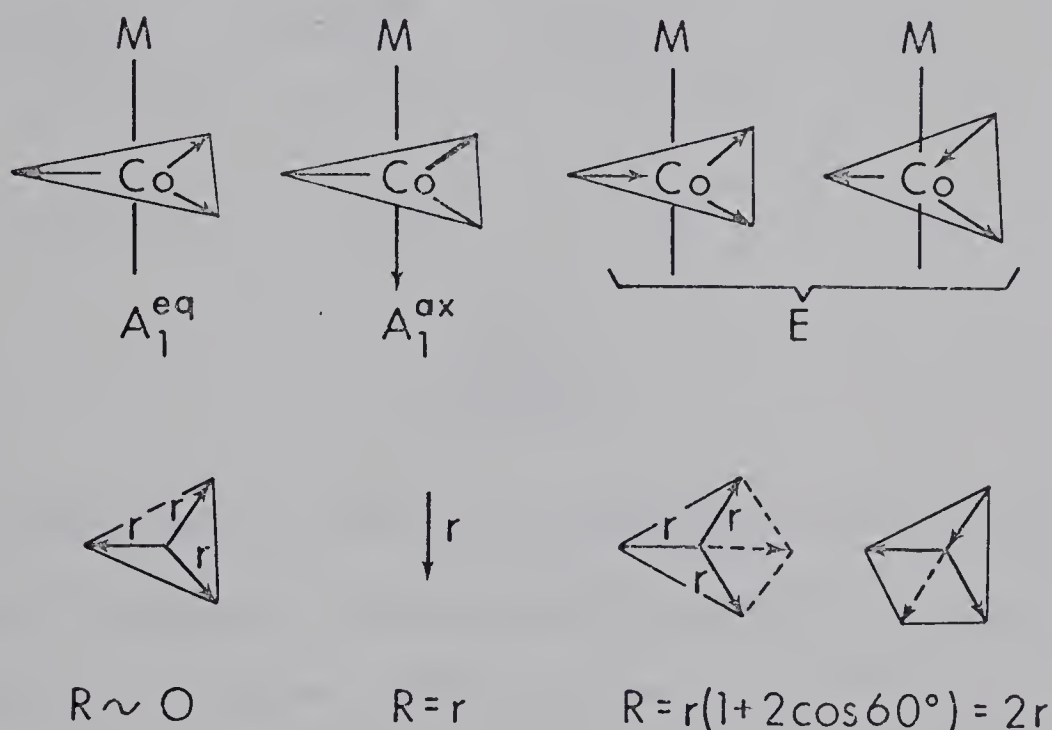
Compounds with C_s symmetry	$\nu(\text{CO}), \text{cm}^{-1}$ ^a			
	$A' (2)$	$A' (1)$	$A' + A''$	
$\text{IPh}_2\text{GeCo}(\text{CO})_4$	2099 (7.9)	2042 (7.2)	2023 (10)	2010 (8.7)
$\text{Cl}_2\text{PhSnCo}(\text{CO})_4$	2108 (9.4)	2054 (8.6)	2033 (9.9)	2021 (10)
$\text{Cl}_2\text{BuSnCo}(\text{CO})_4$	2109 (9.1)	2052 (8.7)	2032 (9.1)	2016 (10)
$\text{Br}_2\text{PhSnCo}(\text{CO})_4$	2106 (9.4)	2052 (7.7)	2032 (9.9)	2020 (10)
$\text{I}_2\text{PhSnCo}(\text{CO})_4$	2102 (8.7)	2048 (6.1)	2028 (10)	2018 (10)
$\text{ClPh}_2\text{SnCo}(\text{CO})_4$	2097 (8.8)	2040 (7.7)	2019 (10)	2004 (8.7)
$\text{ClMe}_2\text{SnCo}(\text{CO})_4$	2095 (9.0)	2037 (7.8)	2013 (10)	1998 (9.9)
$\text{BrPh}_2\text{SnCo}(\text{CO})_4$	2096 (9.0)	2040 (7.6)	2019 (10)	2004 (8.8)
$\text{IPh}_2\text{SnCo}(\text{CO})_4$	2094 (9.5)	2038 (8.1)	2017 (10)	2003 (9.5)
$\text{Cl}(\text{acac})_2\text{SnCo}(\text{CO})_4$	2096 (8.2)	2034 (10)	2022 (9.3)	2009 (9.0)
$\text{Br}_2\text{SbCo}(\text{CO})_4$	2101 (9.5)	2050 (8.2)	2029 (10)	2014 (10)
 PPh_3 Derivatives				
$\text{Br}_3\text{SnCo}(\text{CO})_3\text{PPh}_3$	2056 (0.3)		1999 (10)	
$\text{Cl}_2\text{PhSnCo}(\text{CO})_3\text{PPh}_3$	2046 (1.0)	1988 (9.0)		1972 (10)
$\text{Cl}_2\text{BuSnCo}(\text{CO})_3\text{PPh}_3$	2048 (1.0)	1990 (9.9)		1978 (10)
$\text{Br}_2\text{SbCo}(\text{CO})_3\text{PPh}_3$		1987 (10)		1970 (9.3)
$\text{Br}_2\text{SbCo}(\text{CO})_3\text{PPh}_3^c$	2038 (1.5)	1985 (10)		1969 (9.5)

^a All spectra measured in cyclohexane solution unless otherwise stated. Figures in parentheses are relative heights of bands measured on a linear transmittance scale, taking strongest band as 10.

^b Shoulders, due to decomposition in cell, omitted.

^c In chloroform solution.

dipole moment change of the whole molecule (147). Using this, and assuming that each CO group gives rise to the same dipole moment change on vibration, it is possible to predict the relative intensities which each mode would give rise to. This is shown in XXXV where r is a vector representing the dipole change due to the vibration of an individual CO, and R is the resultant of these vectors. The relative intensities

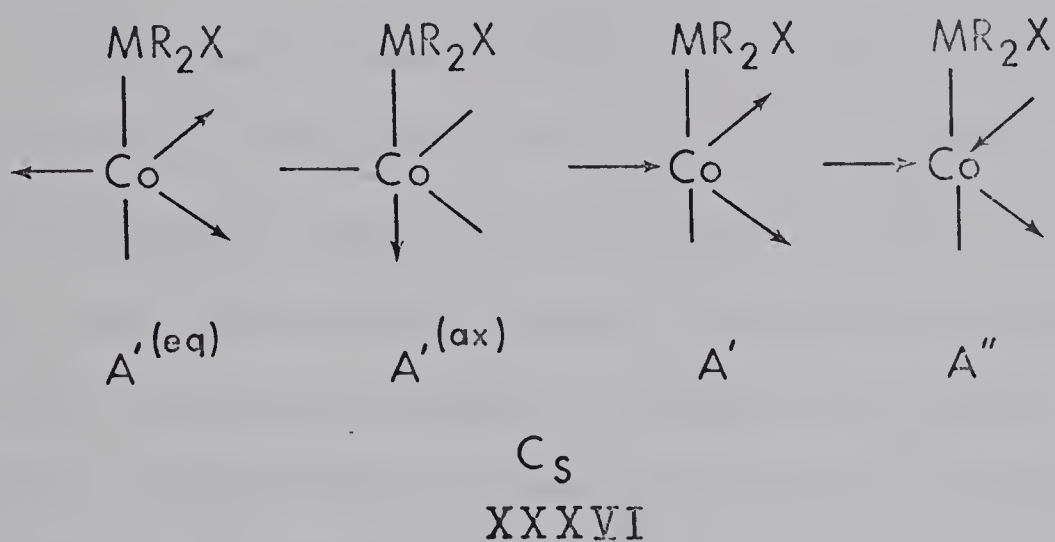


XXXV

of these three modes is then given by comparing ratios of $R^2 : A_1^{eq} : A_1^{ax} : E = 0:1:8$, (there are two degenerate components of the E mode, each of which contribute a relative intensity of 4). This intensity distribution is not exactly observed in practice, however the lowest frequency band is much stronger than the other two, and is therefore assigned to

the E mode. The reason for the discrepancy between observed and predicted modes is discussed in more detail later.

The E mode assignment is strengthened by a consideration of the spectra of the C_s compounds such as $Cl_2PhGeCo(CO)_4$. Four infrared active modes are expected for this symmetry, and are shown in XXXVI. The two modes, $A' + A''$, correspond to

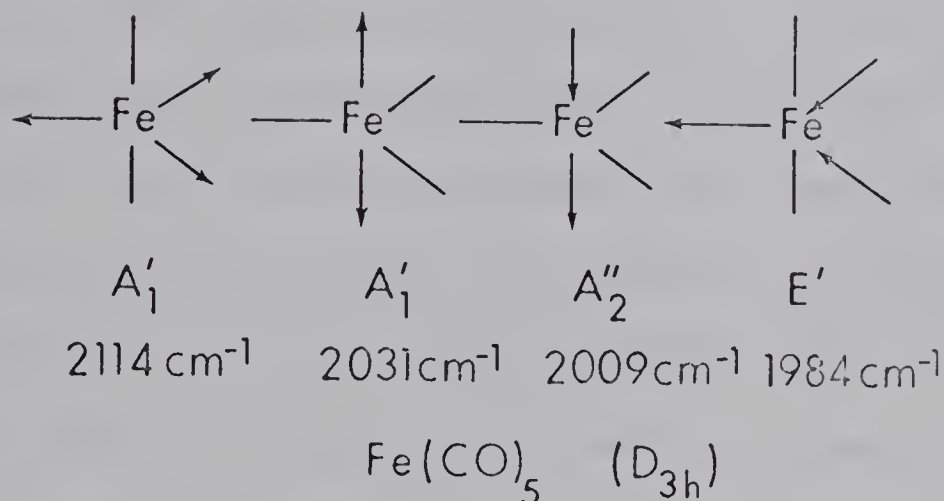
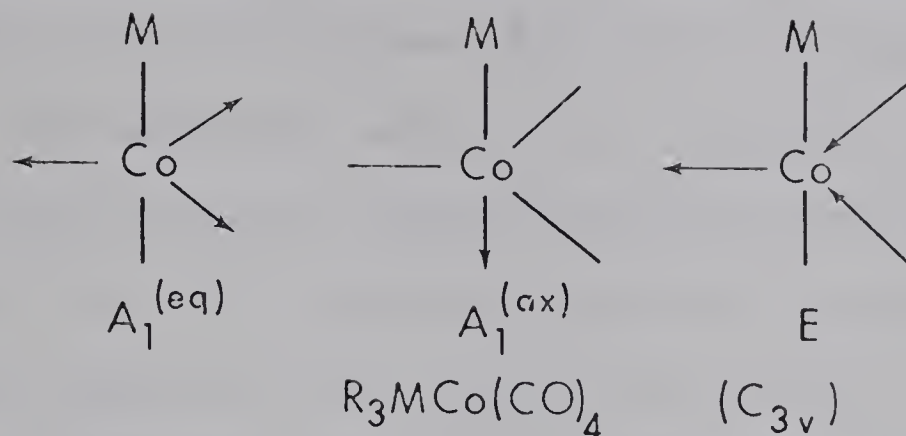


the two degenerate E modes in C_{3v} symmetry, and will possess different frequencies now that the three-fold rotation axis through Co-M is removed. This is observed in all cases of C_s derivatives (Table IX, Figures 9 to 16), the infrared spectra all possessing two relatively close, strong, low frequency bands.

The highest frequency band is assigned to the A_1^{eq} or A'^{eq} mode. The basis for this assignment is the assumption that the mode in which all CO groups are stretching simultaneously will have the highest frequency, as was discussed in the Introduction. The above assignments were also suggested

by other authors, such as Kahn and Bigorgne (148) for $\text{Et}_3\text{MCo}(\text{CO})_4$ ($\text{M} = \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}$) and Hagen and MacDiarmid (149) for various silylcobalt tetracarbonyls. In the case of derivatives of manganese pentacarbonyl, the assignment of the highest frequency band as the totally symmetric stretching mode has been confirmed by force constants measurements (150, 151).

Another way of assigning the $\nu(\text{CO})$ bands of mono(tetracarbonylcobalt) derivatives, is by comparison of the spectra with the observed, and previously assigned $\nu(\text{CO})$ bands of $\text{Fe}(\text{CO})_5$ which has a similar trigonal bipyramidal structure. Orgel (152) used this procedure to assign the infrared spectrum of $\text{PPh}_3\text{PMo}(\text{CO})_5$ by comparison with that of $\text{Mo}(\text{CO})_6$. The assignments of $\text{Fe}(\text{CO})_5$ were made by Raman and infrared studies of the parent carbonyl and phosphine substituted derivatives (153, 154), and are shown in XXXVII below the corresponding modes of $\text{R}_3\text{MCo}(\text{CO})_4$.



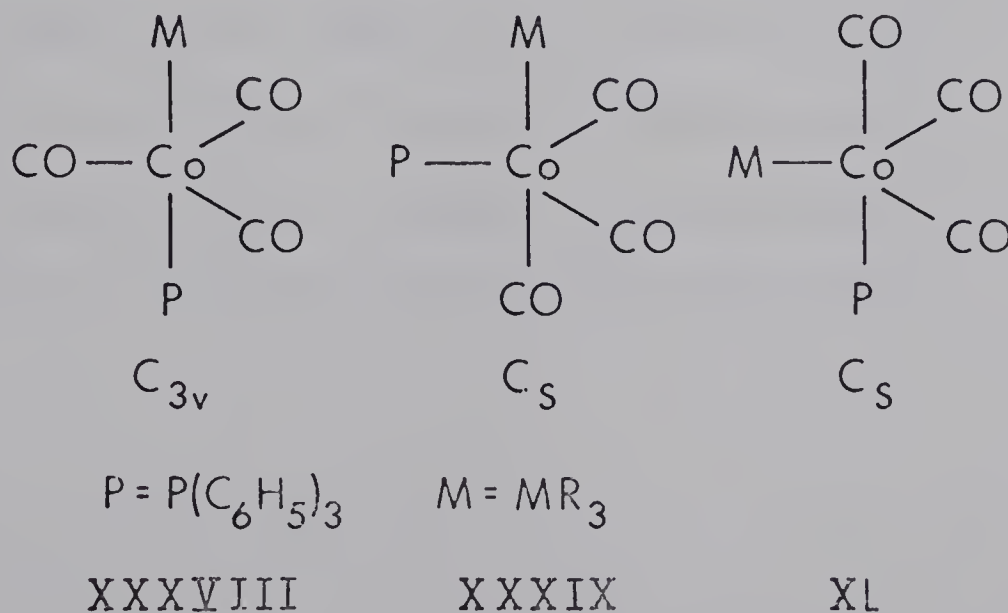
XXXVII

It can be seen that the modes of $Fe(CO)_5$ closely resemble those of $R_3MCo(CO)_4$, thus a similar assignment of the observed bands seems reasonable. The highest frequency band is thus assigned to the A_1^{eq} mode, the lowest to the E mode, and the intermediate frequency band to the A_1^{ax} mode. Kahn and Bigorgne (148) arrived at the same assignments by a similar comparison of $Et_3MCo(CO)_4$ with $Et_3PFe(CO)_4$.

The assignments of all the C_{3v} and C_s derivatives examined are shown in Table IX where $A_1^{(2)}$ (or $A_1'^2$) corresponds

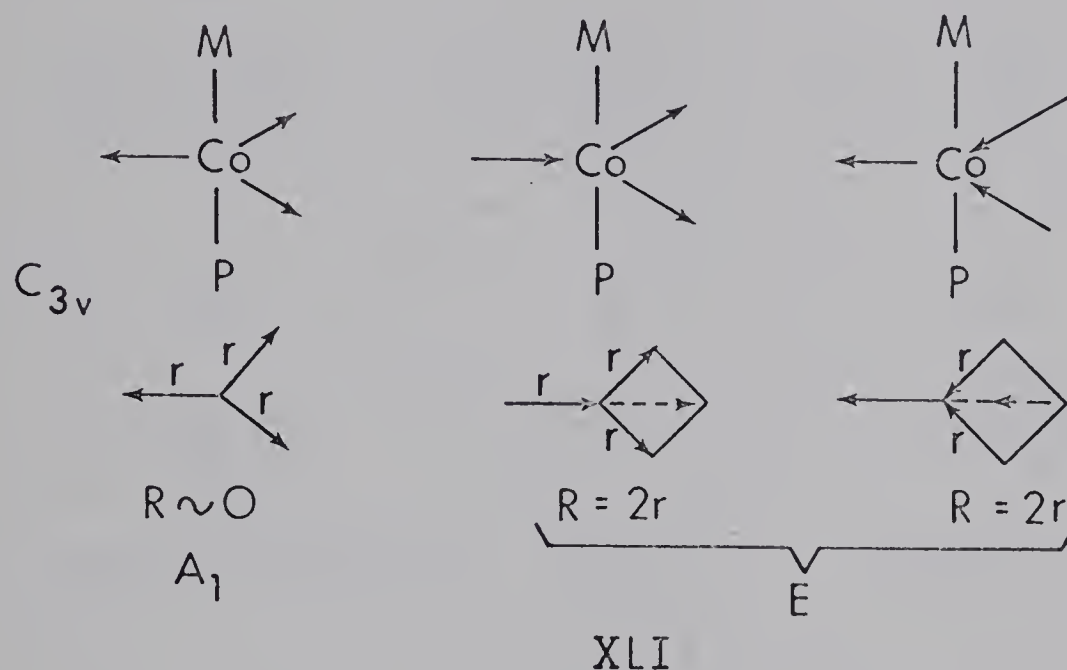
to A_1^{eq} (or A'^{eq}), and $A_1^{(1)}$ (or $A'^{(1)}$) to A_1^{ax} (or A'^{ax}). As mentioned previously, this notation was used because of the possibility of coupling between equatorial and axial vibrations.

The assignments made above are compatible with the infrared spectra of some triphenylphosphine substituted products (Figures 17-20). The tribromotin derivative ($\text{Br}_3\text{SnCo(CO)}_3\text{PPh}_3$) shows one strong band, and one weak band at higher frequency (Figure 17, solid line measured in cyclohexane solution, dotted line in chloroform solution), whereas the derivatives $\text{Cl}_2\text{BuSnCo(CO)}_3\text{PPh}_3$, $\text{Cl}_2\text{PhSnCo(CO)}_3\text{PPh}_3$ and $\text{Br}_2\text{SbCo(CO)}_3\text{PPh}_3$, all show the strong low frequency bands, and one weak high frequency one, (Figures 18-20). The possible structures for an $\text{R}_3\text{MCo(CO)}_3\text{PPh}_3$ molecule are shown in XXXVIII, XXXIX and XL, while the predicted infrared active modes are shown in XLI and XLII. From XLII it can be seen that both XXXIX and XL

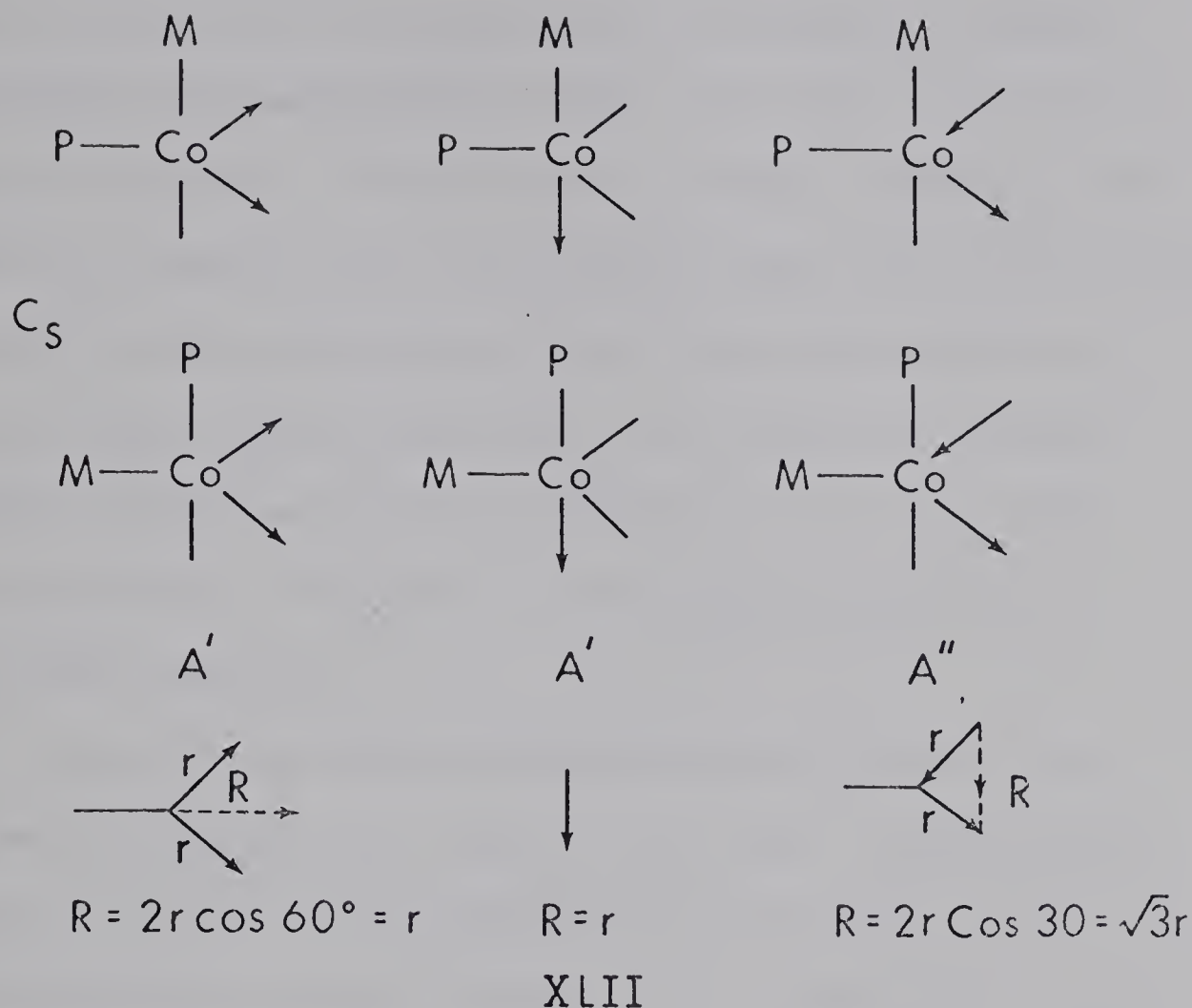


would be expected to give rise to three infrared active bands

in an intensity ratio of $A' : A' : A' = 1:1:3$, whether the group R_3M had a three-fold axis of symmetry or not (both structures being C_s in any case). On the other hand XXXVIII should give rise to two bands in an intensity ratio of $A_1:E = \sim 0:8$, i.e. one very weak and one strong. Furthermore, replacing an R_3M



group by X_2RM will reduce the symmetry from C_{3v} to C_s and remove the degeneracy of the E mode, thus two strong and one weak band would be expected. The observed spectra therefore strongly favour structure XXXVIII; again the highest frequency band is assigned to the equatorial A mode, and the very strong low frequency band to the E mode.



(ii) Effect of R_3M on the Stretching Frequencies

It has been noted previously by various authors that the value of the carbonyl stretching frequency of $LM(CO)_x$ is dependent upon the nature of L. Thus Abel et al. (155) noted a very pronounced shift of $\nu(CO)$ to lower wavenumbers in the series $(Ph_nPCl_{3-n})_3Mo(CO)_3$ as n increased from 0 to 3. This he ascribed to a reduction of the d_π acceptor properties of phosphorous as the electronegativity of the groups on P is reduced. Later, Kasenally et al. (21) noted a similar trend for some $LMn(CO)_5$ derivatives. They plotted the CO stretching

frequency against the electronegativity of L (where L = Cl, Br, I (O-Triars)Cu, (O-Triars)Ag and (O-Triars)Au) obtained a straight line relationship for A_1^{eq} , and a non-linear relation for the other modes. Very recently, Thompson and Graham (156) reported a similar linear relationship between $A_1^{(2)}$ ("equatorial" A mode) and the electronegativity of groups attached to tin for the series $Ph_n Cl_{3-n} SnMn(CO)_5$, and by use of this graph obtained values for the electronegativity of the C_6F_5 group by fitting the $\nu(CO)$ values of the $Ph_n (C_6F_5)_{3-n} SnMn(CO)_5$ series onto the line.

In the present work the same effect was observed for the series $X_n R_{3-n} MCo(CO)_4$ where M = Sn or Ge. A plot of the sum of the Pauling electronegativities of halogens attached to M against the frequency of the A_1 or A' modes gave straight lines as shown in Figures 46 and 47. In both cases there was a tendency for the lines to split into three, -different halogens lying on different lines; this was more pronounced for the tin derivatives. A similar, though non-linear, dependence was observed between the sum of halogen electronegativities and the mean carbonyl stretching frequencies, $\nu(CO)_m$, given by $1/4[\nu(A_1^{(2)}) + \nu(A_1^{(1)}) + 2\nu(E)]$ or $1/4[\nu(A'^{(2)}) + \nu(A'^{(1)}) + \nu(A') + \nu(A'')]$, where the terms in square brackets represent the observed frequencies of the corresponding modes. This is shown in Figures 48 and 49. Finally, in order to take into account the electron withdrawing

properties of the organic groups, the sum of the inductive Taft functions (157) of all the groups attached to M were plotted against the mean frequencies, as shown in Figures 50 and 51. These results indicate a marked dependence of $\nu(\text{CO})$ on the electron withdrawing properties of R_3M .

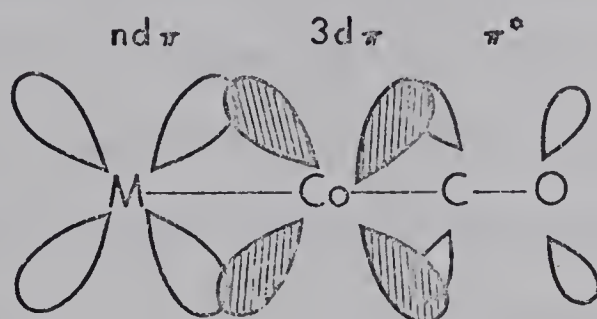
In order to attempt to explain the above results, at least in a qualitative fashion, a brief discussion of the bonding in these derivatives is necessary. It is now well accepted that the bonding of CO to a metal involves donation of a lone pair of electrons on carbon into an empty metal hybrid, accompanied by back donation by filled metal d orbitals into empty carbonyl π^* orbitals (158). This partial occupation of the carbonyl antibonding π^* orbitals by electrons from the filled metal d_π orbitals will decrease the π bonding between C and O resulting in a bond order below three. In other words, increasing M-C bonding decreases C-O π bonding. This reduction of C-O bond order is reflected in the $\nu(\text{CO})$ which are usually lower than observed for free CO (158). It is usually assumed that variations in $\nu(\text{CO})$ reflect only variations in C-O π bonding, and thus in M-C π bonding. This assumption has been given weight by overlap integral calculations which indicate that vibration of a CO group causes a much larger change in π overlap, than in σ overlap (159).

In the derivatives under discussion, a cobalt atom is

bonded both to a main group metal and to carbonyl groups.

The d_{π} electron density of cobalt can thus donate into unfilled germanium or tin d orbitals, as well as into $CO \pi^*$ orbitals.

This situation is represented in XLIII. The observed variation of $\nu(CO)$ can now be discussed in terms of variations of $d_{\pi} \rightarrow \pi^*$ overlap between Co and C. There are two ways in



XLIII

which this can be influenced by R_3M ; one involving changes in $Co-M\pi$ bonding, and the other involving contraction of filled Co d orbitals by an inductive effect via the $M-Co \sigma$ bond.

Both of these effects have been discussed in detail by Graham (160). Considering first the π effect, increasing the electronegativity of groups attached to M will contract the M d orbitals and increase their ability to accept d_{π} electron density from Co, as discussed by Abel et al (155) for PCl_3 complexes. This increase in $Co-M\pi$ overlap will transfer d_{π} electron density away from the $CO \pi^*$ orbitals and hence increase the $C-O \pi$ bond order with a resulting increase in $\nu(CO)$. The inductive (or σ) effect involves a withdrawal

of electrons along the M-Co bond as the electronegativity of groups on M increases. This electron withdrawal will contract the Co d orbitals, and again decrease donation of Co d_π electrons into CO π* orbitals, thus increasing ν(CO). Both effects thus operate in the same direction. The observed trends to higher wavenumbers as the electronegativity is increased, as shown in Figures 46 to 51, may therefore be explained in terms of a combination of σ and π effects.

It was also observed that ν(CO) for the compounds Ph₃MCo(CO)₄ shifted to lower values as M varied from Si to Pb, as shown below:

		ν(CO)		
Ph ₃ SiCo(CO) ₄	(161)	2093	2032	2003
Ph ₃ GeCo(CO) ₄		2091	2030	2006
Ph ₃ SnCo(CO) ₄		2087	2027	1999
Ph ₃ PbCo(CO) ₄		2081	2022	1997

Thus, in spite of the irregular variation of electronegativity of M, it appears that the combination of π- and σ- withdrawal decreases monotonically from Si to Pb.

The influence of the nature of R₃M on ν(CO) was also noted very recently by Kahn and Bigorgne (148) who studied the series Et₃MCo(CO)₄ (where M = Si, Ge, Sn and Pb) and R₃SiCo(CO)₄. These authors observed trends very similar to the present work when M and R were varied. They also explained these trends in terms of σ and π effects, although, in the case of Et₃MCo(CO)₄, they concluded that variation of M affected ν(CO) via the π

effect only, σ effects being very small due to the similarity in electronegativity of Si, Ge, Sn and Pb. They also studied the dipole moments of these compounds and were able to obtain values for the $M-\text{Co}(\text{CO})_4$ bond dipole. All of the $\text{Et}_3\text{MCo}(\text{CO})_4$ compounds possessed bond dipole moments (1.67D for Si, and 3.05D for Pb) which indicated that Et_3M groups were electron donors to the $\text{Co}(\text{CO})_4$ group, whereas the dipole moment of $\text{Cl}_3\text{SiCo}(\text{CO})_4$ indicated the strong electron-withdrawing properties of the Cl_3Si group. Furthermore, they found a linear relationship between the mean carbonyl stretching frequency and the bond dipole moment, emphasizing the influence of electron withdrawing ability of R_3M upon Co-C π bonding (and thus on $\nu(\text{CO})$ frequency). By using this relationship they were able to arrive at a rough value for the electronegativity of the $\text{Co}(\text{CO})_4$ group. They pointed out that the mean frequency for $\text{Me}_3\text{CCo}(\text{CO})_4$, when plotted on the graph, indicated a bond moment of zero; as the carbon atom is very unlikely to be a π acceptor, they concluded that the $\text{Co}(\text{CO})_4$ group has an electronegativity very close to that of the CMe_3 group (2.5 on Pauling's scale).

By making use of force constants calculated using the Cotton Kraihanzel procedure (150), Graham (160) has attempted to separate the π and σ effects. This was done by assuming that σ withdrawal operates isotropically on all five CO groups, whereas the change in the π -acceptor property in going from

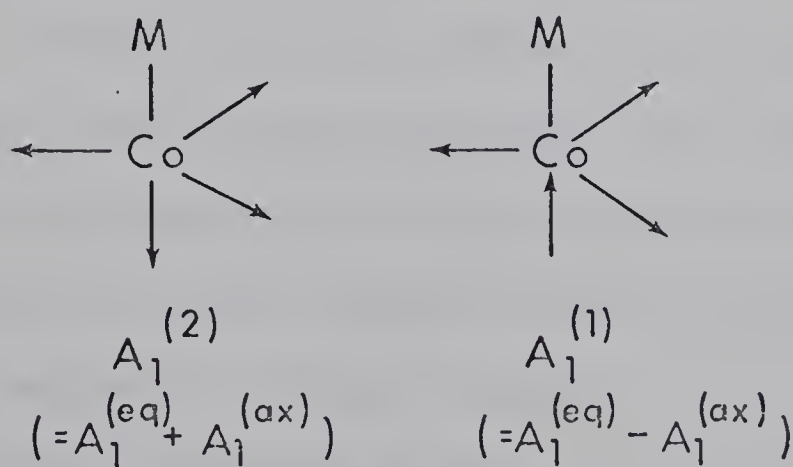
L to L' will affect Δk_1 more than Δk_2 by a factor of two, where Δk_1 is the change in the axial CO stretching force constant, and Δk_2 the change in the equatorial force constant. Using these relationships, it was possible to calculate a set of σ and π parameters for various ligands relating the σ - and π -withdrawing (or acceptor) properties to those of the Me group in MeMn(CO)_5 , chosen as a standard. In general it was found that Ph_3M groups (M = Si, Ge, Sn and Pb) were both fairly strong π -acceptors and σ donors, whereas X_3M groups were very weak σ donors or acceptors, but had similar π -acceptor properties to the Ph_3M ligands. This was explained in terms of halogen back donation to M. Replacing phenyl groups by halogens increased σ withdrawal (or decreased σ donation), but the expected trend of increasing Mn-M π overlap as the electronegativity of X increased was reversed by increasing halogen to M π overlap which reduced the availability of M d_π orbitals for Mn-M π bonding.

(iii) Intensities of the A_1 (or A') Bands

It was pointed out earlier that the observed relative intensities of the two high frequency A modes are inconsistent with the intensities predicted for pure axial or equatorial stretching modes. In particular, the highest frequency A_1^{eq} (or A'^{eq}) should possess zero or very low intensity, and A_1^{ax} medium intensity (see XXV), whereas, in practice, both bands possess medium intensity. This is shown in Table IX where the

relative heights of the observed bands on a percent transmission scale are recorded.

There are several ways in which the A^{eq} band can gain intensity. The first involves coupling of the axial and equatorial modes, as shown in XLIV, giving two different modes $A_1^{(2)}$ and $A_1^{(1)}$ which both involve stretching of all four CO groups, and can be represented by linear combinations of A_1^{eq} and A_1^{ax} . The extreme case in which both equatorial and axial vibrations combine equally is shown in XLIV, and both would be expected to give rise to equally intense bands. Therefore, as the degree of coupling is increased, the relative intensity of these two modes would increase from zero to one.



XLIV

The A modes could also change relative intensity by means of a distortion of the three equatorial CO groups towards or away from R_3M , so that the M-Co-C angle is no longer 90° . This will result in increase in intensity of the equatorial mode. Resolving the three oscillating dipole vectors along the axis,

we obtain $R = 3r\cos\theta$ where $\theta = \angle M-Co-C$, R = resultant, and r = dipole change when one CO group vibrates. The ratio of the relative intensities of $A^{eq}:A^{ax}$ will then be given by $9\cos^2\theta:1$, thus, for the two intensities to be equal $\theta = 71.1^\circ$. However, from X-ray structural studies of $Co(CO)_4$ derivatives, θ is found to lie in the range $82-85^\circ$, e.g. in $Cl_3SiCo(CO)_4$, $\theta = 84^\circ$ (68), and in $Hg[Co(CO)_4]_2$, $\theta = 82^\circ$ (8); distortions of this kind alone are therefore insufficient to account for the observed intensities (assuming that θ does not change in solution). It is therefore probable that coupling, or a combination of coupling and distortion, is responsible for the observed intensities. This conclusion was also reached by Kahn and Bigorgne (148) from intensity measurements on $Et_3MCo(CO)_4$. It should be noted, however, that in absence of both coupling and equatorial distortion, the equatorial A_1 mode could still possess some intensity because of an unequal movement of electron density towards or away from cobalt as the equatorial carbonyls vibrate.

A discussion of the relative intensities of the A_1 modes of $LMn(CO)_5$, in terms of both coupling and distortion, was given by Manning and Miller (162). They calculated the degree of coupling between the two A_1 modes for $XM(CO)_5$ ($X = Cl, Br, I, H$, and $M = Mn, Tc, Re$), and showed that the order of increase of the ratio of intensities of $A_1^{(2)}$ to $A_1^{(1)}$ ($I > Br > Cl > H$) was different from the order of increase of coupling ($H > I > Br > Cl$).

Furthermore, the intensity ratios among the halogen complexes varied much more than did the coupling. These results they explained on the basis of a variation of θ as well as coupling. In $\text{HMn}(\text{CO})_5$ the intensity ratio is almost zero, whereas the coupling is large. However, they were able to show that by taking into account the value of θ ($= 83^\circ$), the very low intensity could be explained. Similarly the rapid increase in ratio for the halogen compounds was explained by an increase in θ in the order $\text{Cl} < \text{Br} < \text{I}$, consistent with increasing repulsion between halogen and radial carbon atoms.

A more detailed treatment of these derivatives by Brateman, Bau and Kaesz (163) appeared more recently, using the improved vibrational analysis of Kaesz et al. (151) and the accurate absorption data obtained by Abel and Butler (164). In the previous work of Manning and Miller it was assumed that unit extension of both equatorial and axial CO groups gave rise to the same dipole change, i.e. that their dipole moment derivatives, μ , were equal. However, because of the different environments of the two sets of CO groups, this assumption is not necessarily valid. By using the improved vibrational analysis and absorption measurements, Brateman et al. were able to relate the observed intensity and the calculated force constants to θ and the axial and equatorial dipole moment derivatives μ_a and μ_r . In this way they were able to calculate θ , μ_a and μ_r for $\text{XMn}(\text{CO})_5$ and

and $\text{XRe}(\text{CO})_5$. Their results showed in general that $\mu_a/\mu_r \gg 1$ and varied between 1.04 for $\text{HMn}(\text{CO})_5$ and 1.67 for $\text{IMn}(\text{CO})_5$. The calculated value of θ for $\text{HMn}(\text{CO})_5$ was very close to the value determined for the solid state, while values of θ of $90 \pm 3^\circ$ for the halides were at least reasonable.

The factors influencing the intensities of carbonyl stretching vibrations have also been discussed in some detail by Brown and Darensbourg (174).

Relating these results to the present case, it seems probable that a combination of coupling, distortion and a difference of μ_r and μ_a must all be taken into consideration when discussing tetracarbonylcobalt derivatives. However, lack of accurate absorption data and vibrational analysis for these derivatives preclude any attempts to separate these three factors.

A very interesting correlation was observed between the mean of the A_1 frequencies and the ratio of absorbances of these two bands for the series $\text{X}_n\text{R}_{3-n}\text{MCo}(\text{CO})_4$. This is illustrated in Figure 52. Four parallel straight lines were obtained corresponding to each of the four sets of compounds: $\text{Ph}_3\text{MCo}(\text{CO})_4$, $\text{XR}_2\text{MCo}(\text{CO})_4$, $\text{X}_2\text{RMCo}(\text{CO})_4$ and $\text{X}_3\text{MCo}(\text{CO})_4$, where $\text{M} = \text{Ge}$ or Sn . The reason for this relationship between the absorbance ratio and $\nu(\text{CO})$

is not completely clear at present. Possibly variations of relative intensity reflect changes in coupling between the equatorial and axial modes. Such coupling presumably occurs via Co-C π bonding, so that anything which influences this will affect coupling. The mean frequency will also be dependent upon Co-C π bonding. This would explain the observed trend for any one series, but not the fact that four different lines were obtained. Attempts to explain the observed results in detail must await detailed vibrational studies and accurate absorption data, as well as further structural determinations, in order to allow for the influence of μ_a/μ_r and θ on intensity.

2. Infrared Spectra of Bis- and Tris(tetracarbonylcobalt)

Derivatives

The infrared spectra in the $\nu(\text{CO})$ region for all the bis derivatives prepared in this work are recorded in Table X, and typical spectra are shown in Figures 21 to 34. Compounds with C_{2v} symmetry, such as $\text{Ph}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$, are expected to possess a maximum of seven infrared active vibrational modes ($2A_1 + 3B_1 + B_2$), whereas those with C_s symmetry, such as $\text{ClPhSn}[\text{Co}(\text{CO})_4]_2$, should have a maximum of eight ($4A' + 4A''$) (XLV). The observed bands are in good agreement these predictions in the case of $\text{R}_2\text{M}[\text{Co}(\text{CO})_4]_2$ and $\text{RXM}[\text{Co}(\text{CO})_4]_2$ ($\text{M} = \text{Ge}, \text{Sn}$) as indicated by Table X, and illustrated in Figures 24, 27, 28 and 31 for the C_{2v} compounds, and Figures 32 to 34 for

TABLE X

Infrared Carbonyl Stretching Frequency Data

for Bis and Tris[tetracarbonylcobalt] Derivatives

Compounds with C_{2v} symmetry	$\nu(\text{CO}), \text{cm}^{-1}$	$(3A_1 + 3B_1 + B_2)^a$
$(\text{THF})_2\text{Cd}[\text{Co}(\text{CO})_4]_2$	2070 (3.4) 2054 (10) 1990 (8.4) 1978 (9.5) 1960 (10) 1948 (sh. 5.6)	
$(\text{acac})\text{Ga}[\text{Co}(\text{CO})_4]_2$	2094 (1.2) 2076 (9.5) 2027 (1.9) 2020 (7.4) 2010 (8.9) 2000 (10) 1988 (5.0)	
$(\text{acac})\text{In}[\text{Co}(\text{CO})_4]_2$	2094 (1.9) 2076 (9.4) 2027 (2.0) 2020 (4.9) 2003 (10) 1991 (4.9) 1959 (0.2)	
$\text{Cl}_2\text{Ge}[\text{Co}(\text{CO})_4]_2$	2117 (0.1) 2100 (9.6) 2058 (6.7) 2054 (3.8) 2044 (10) 2026 (4.4) 2016 (2.4)	
$\text{I}_2\text{Ge}[\text{Co}(\text{CO})_4]_2$	2113 (4.1) 2096 (10) 2054 (7.5) 2051 (5.6) 2042 (10) 2025 (5.4) 2013 (2.9)	
$\text{Me}_2\text{Ge}[\text{Co}(\text{CO})_4]_2$	2098 (3.5) 2081 (9.8) 2033 (3.5) 2027 (7.4) 2019 (9.8) 2006 (10) 1997 (7.2)	
$\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$	2114 (0.1) 2097 (9.9) 2056 (6.6) 2052 (3.8) 2040 (10) 2023 (5.2) 2016 (3.8)	
$\text{Br}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$	2113 (0.1) 2096 (9.7) 2055 (4.5) 2050 (2.8) 2040 (10) 2026 (3.3) 2016 (2.2)	
$\text{I}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$	2110 (3.5) 2093 (9.6) 2053 (5.1) 2048 (3.6) 2037 (10) 2021 (4.4) 2012 (2.6)	
$\text{Me}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$	2095 (3.7) 2078 (10) 2031 (1.9) 2024 (5.4) 2013 (8.8) 2002 (9.5) 1992 (6.0)	
$\text{Ph}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$	2095 (5.1) 2080 (9.9) 2033 (4.0) 2029 (7.4) 2018 (10) 2009 (9.7) 1995 (7.3)	
$\text{Vn}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$	2097 (4.6) 2080 (10) 2037 (3.7) 2028 (6.8) 2018 (9.6) 2009 (9.7) 1998 (7.4)	

TABLE X (continued)

Compounds with C_s symmetry	$\nu(\text{CO}), \text{cm}^{-1} (4A' + 4A'')$ ^a									
$\text{BrGa}[\text{Co}(\text{CO})_4]_2 \cdot \text{THF}$	2091 (3.4)	2077 (10)	2032 (5.6)	2024 (6.5)	2012 (10)	2004 (10)	1992 sh.	1980 sh.		
$\text{BrIn}[\text{Co}(\text{CO})_4]_2 \cdot \text{THF}$	2092 (3.2)	2076 (10)	2030 (4.2)	2022 (4.7)	2009 (9.4)	2003 (9.2)	1991 sh.	1982 sh.		
$\text{IMeGe}[\text{Co}(\text{CO})_4]_2$	2106 (2.9)	2089 (10)	2046 (4.3)	2040 (4.4)	2030 (9.0)	2024 (9.2)	2014 (4.9)	2000 (2.9)		
$\text{ClMeSn}[\text{Co}(\text{CO})_4]_2$	2104 (3.0)	2088 (10)	2044 (3.7)	2038 (4.0)	2022 (8.7)	2017 (8.8)	2005 (5.5)	1996 (3.5)		
$\text{ClPhSn}[\text{Co}(\text{CO})_4]_2$	2105 (3.3)	2088 (10)	2045 (4.8)	2039 (4.5)	2030 (9.0)	2021 (8.7)	2014 (5.7)	1999 (2.9)		
$\text{ClBuSn}[\text{Co}(\text{CO})_4]_2$	2103 (3.3)	2086 (10)	2044 (4.4)	2037 (3.9)	2024 (8.4)	2018 (8.7)	2007 (5.4)	1996 (3.1)		
$\text{ClVnSn}[\text{Co}(\text{CO})_4]_2$	2106 (4.3)	2088 (10)	2046 (6.6)	2040 (6.1)	2029 (9.6)	2022 (9.7)	2012 (7.4)	2000 (4.6)		
Other Compounds										
$\text{Cd}[\text{Co}(\text{CO})_4]_2$	2070 (5.8)	2015 (2.3)	1993 (10)							
$(\text{acac})_2\text{Sn}[\text{Co}(\text{CO})_4]_2$	2101 (0.6)	2091 (3.3)	2088 (3.5)	2069 (10)	2023 (7.7)	2020 sh.	2013 (8.0)	2003 (8.3)		
$(\text{AcO})_2\text{Sn}[\text{Co}(\text{CO})_4]_2$	2112 (1.6)	2106 (0.4)	2093 (9.0)	2088 sh.	2066 (10)	2044 (9.0)	2030 sh.	2024 (10)		
	2019 sh.									
Tris Derivatives C_{3v} symmetry										
$\text{Tl}[\text{Co}(\text{CO})_4]_3$	2069 (10)	2007 (5.0)								

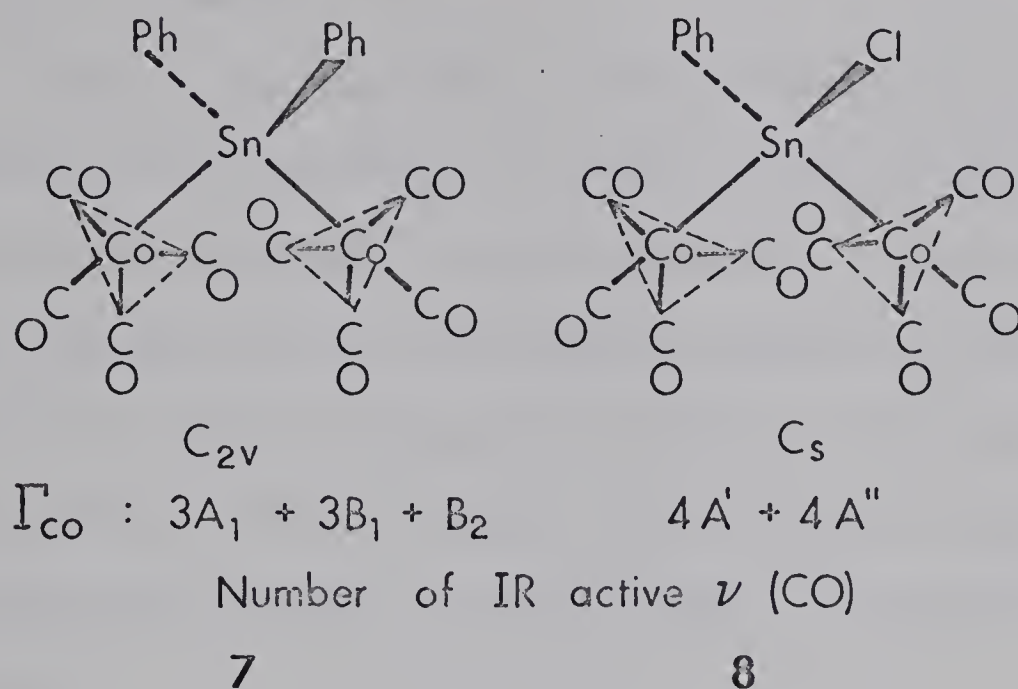
TABLE X (continued)

Tris Derivatives C _{3v} symmetry	$\nu(\text{CO}), \text{cm}^{-1}$									
FSn[Co(CO) ₄] ₃	2087 (10)	2049 (5.2)	2041 (1.5)	2026 (10)	2006 sh.					
ClSn[Co(CO) ₄] ₃	2110 (0.5)	2088 (10)	2049 (6.0)	2043 sh.	2028 (9.7)	2001 (3.6)				
BrSn[Co(CO) ₄] ₃	2108 (0.7)	2086 (10)	2048 (7.0)	2042 (3.7)	2026 (9.7)	2000 (4.6)				
ISn[Co(CO) ₄] ₃	2108 (0.6)	2085 (10)	2047 (3.5)	2041 (1.2)	2026 (8.3)	2000 (1.6)				
MeSn[Co(CO) ₄] ₃	2101 (0.6)	2079 (10)	2028 sh.	2020 (8.9)	2010 (9.1)	1992 (1.4)				
BuSn[Co(CO) ₄] ₃	2100 (2.1)	2078 (10)	2029 sh.	2019 (9.5)	2008 (9.7)	1988 (2.5)				
PhSn[Co(CO) ₄] ₃	2102 (2.2)	2079 (10)	2037 sh.	2023 (9.3)	2010 (8.3)	2000 (3.6)				
VnSn[Co(CO) ₄] ₃	2102 (1.2)	2080 (10)	2029 sh.	2022 (9.0)	2012 (9.5)	1997 (2.2)				
AcOSn[Co(CO) ₄] ₃	2110 (0.8)	2086 sh.	2084 (9.7)	2049 (2.7)	2040 (4.0)	2025 (10)	2021 sh.	2008 (3.2)		
	1998 (2.5)									
Bi[Co(CO) ₄] ₃	2091 (1.1)	2074 (10)	2020 (5.3)	2008 (5.3)						
Sn[Co(CO) ₄] ₄	2079 (9.8)	2032 (3.0)	2018 (10)	1999 sh.	1994 (2.3)					

^a Infrared spectra measured in cyclohexane unless otherwise stated.

Figures in parentheses are relative heights of bands measured on a linear transmittance scale.

the C_s derivatives. The spectra of $X_2M[Co(CO)_4]_2$, where $M = Ge, Sn$ and $X = Cl, Br, I$, however, are somewhat



XLV

different, in terms of relative band positions and intensities, from the organotin or organogermanium derivatives, as illustrated by Figures 23, 25 and 26. In the case of the tin derivatives, however, seven bands can still be counted, if shoulders are included. The reason for this difference is not clear, although it may possibly reflect different degrees of coupling between the various modes which have the same symmetry.

That the number of bands predicted on the basis of the overall molecular symmetry is observed in practice, indicates that it is not possible to predict the number of bands on the basis of the local symmetry of the $Co(CO)_4$ groups, as such a treatment would lead to a prediction of four bands for both C_{2v} and C_s derivatives. In other words, the $Co(CO)_4$ groups

cannot be regarded as isolated from each other, but may be thought of as coupled together across the main group metal via $d_{\pi} - d_{\pi} - d_{\pi}$ overlap.

Owing to the complexity of the infrared spectra of these compounds it is not possible to assign all the observed bands unambiguously. However, it seems reasonable to assign the highest frequency band to the totally symmetric A_1 mode in which all eight CO groups are stretching simultaneously, in the same way that the highest frequency band in $R_3MCo(CO)_4$ derivatives are assigned to the $A_1^{(2)}$ mode, as previously discussed.

The infrared spectra of the tris(tetracarbonylcobalt)tin(IV) derivatives are recorded in Table X, and typical spectra are reproduced in Figures 35 to 37. The molecules can reasonably be taken as having C_{3v} symmetry, regarding all organic groups as point groups. Seven infrared-active bands are predicted for this symmetry, $(3A_1 + 4E)$ and in most cases seven can be counted including shoulders. Owing to the complexity of these molecules, no attempt to assign the observed bands will be made, except to suggest that the highest frequency band may be due to the totally symmetric stretching of all twelve CO groups. The spectra of pure $Tl[Co(CO)_4]_3$ and $Bi[Co(CO)_4]_3$ could not be obtained owing to rapid decomposition in the infrared cell with formation of $Co_2(CO)_8$. The bands reported in Table X were obtained by subtracting the

spectrum of $\text{Co}_2(\text{CO})_8$ from the observed bands so that it is possible that relatively weak bands were obscured.

The spectrum of $\text{Sn}[\text{Co}(\text{CO})_4]_4$ is shown in Figure 38, and is seen to consist of two very strong and three weak bands, including a weak shoulder. This result seems to indicate that the symmetry of the molecule in solution is not strictly T_d for which a maximum of three infrared-active bands would be predicted. Rotation of one $\text{Co}(\text{CO})_4$ group through 60° would reduce the symmetry from T_d to C_{3v} and give a sterically more favourable conformation. It is of interest that the general appearance of the spectrum of this compound is similar, except for intensity differences, to that of $\text{ClSn}[\text{Co}(\text{CO})_4]_3$ which has C_{3v} symmetry at most.

3. Infrared Spectra of Other Transition Metal Derivatives

The $\nu(\text{CO})$ bands observed for main group metal derivatives of transition metals other than cobalt are included in Table XI, and a selection reproduced in Figures 42 to 45.

The spectrum of $\text{I}_2\text{InFe}(\text{CO})_2\text{Cp}\cdot\text{THF}$ is of interest, as it possesses four $\nu(\text{CO})$ bands, whereas a maximum of two would be expected for this molecule. Similar results have been obtained for other $\text{Fe}(\text{CO})_2\text{Cp}$ derivatives, and is thought to be due to the presence of conformers in solution. Thus Jetz and Graham (165) observed two sharp bands for $\text{Cl}_3\text{SiFe}(\text{CO})_2\text{Cp}$, but when the three-fold axis of rotation through Si was removed in the

TABLE XI

Infrared Carbonyl Stretching Frequencies of Miscellaneous Compounds

Compound	$\nu(\text{CO}), \text{cm}^{-1}$ ^a				
$\text{Br}_3\text{In}_3\text{Co}_4(\text{CO})_{16}$	2097 sh.	2089 (10)	2055 (4.6)	2035 (5.3)	
	2025 (7.2)	2012 (6.3)	2000 sh.		
$(\text{acac})_2\text{SnCo}_2(\text{CO})_7$	2076 (6.6)	2036 (10)	2013 (9.8)	2004 (8.8)	
	1994 (8.3)	1836 (5.9)			
$\text{BiCo}_3(\text{CO})_{10}$	2090 (6.1)	2043 (10)	2024 (7.8)	2014 (6.0)	
	1882 (5.8)				
$\text{I}_2\text{Ge}[\text{NiCOCP}]_2$	2050 (7.1)	2028 (10)			
$\text{Cl}_2\text{Sn}[\text{NiCOCP}]_2$	2043 (10)	2019 (10)			
$\text{Br}_2\text{GaMn}(\text{CO})_5$	2102 (4.3)	2052 (5.3)	2036 sh.	2005 (10)	
$\text{Br}_2\text{InMn}(\text{CO})_5$	2098 (5.1)	2034 (2.9)	2014 (9.8)	2001 (10)	
	1990 sh.				
$(\text{acac})\text{In}[\text{Mn}(\text{CO})_5]_2$	2098 (0.4)	2067 (3.8)	1998 (10)	1977 (2.6)	
	1956 (0.2)				
$\text{I}_2\text{InFe}(\text{CO})_2\text{Cp} \cdot \text{THF}$	2004 (9.5)	1996 (10)	1957 (7.2)	1950 (9.5)	
$\text{I}_2\text{InMo}(\text{CO})_3\text{Cp} \cdot \text{THF}$	2006 (10)	1938 (3.5)	1914 (8.0)		

^a Infrared spectra measured in cyclohexane solution unless otherwise stated.

Figures in parenthesis are relative heights of bands measured on a linear transmittance scale.

compound $\text{MeCl}_2\text{SiFe(CO)}_2\text{Cp}$, both bands were split into two. The reason for this was felt to be due to the presence of two different rotational conformers in which the Me or Cl groups of the MeCl_2Si group are taking different positions relative to the positions of the CO groups by rotation about the Si-Fe bond. In the present case, rotation of the $\text{THF}\cdot\text{I}_2\text{In}$ group about the In-Fe bond could similarly produce different rotational conformers with slightly different values of $\nu(\text{CO})$.

B. Mass Spectra

INTRODUCTION

With the advent of commercially available high resolution mass spectrometers capable of handling compounds with molecular weights of 1000 or more, increasing use is being made of the mass spectra of organometallic compounds and transition metal complexes as a means of characterizing these compounds. The mass spectra of numerous mono- and polynuclear carbonyls have been investigated by several authors, and it has been shown that such compounds have a tendency to lose carbonyl groups stepwise in the mass spectrometer. This has been demonstrated for the mono-nuclear derivatives $M(CO)_x$ ($x = 6$, $M = Cr, Mo$ or W ; (166) $x = 5$, $M = Fe$; (167) $x = 4$, $M = Ni$ (167)) for which the fragments $M(CO)_n^+$ ($n = 0$ to x) were observed, and for $Co_2(CO)_8$ and $Mn_2(CO)_{10}$ (168) where similar stepwise loss of CO occurred.

More recently, King (169) reported the mass spectra of some polynuclear metal carbonyl derivatives, such as $Co_4(CO)_{12}$, $Ru_3(CO)_{12}$ and $YCo_3(CO)_9$, where ions corresponding to consecutive loss of CO groups, together with bare metal ions such as Co_4^+ , were observed. Other examples of the use of mass spectroscopy include the work of Smith et al. (170) who used mass spectroscopy to confirm the composition of some

polynuclear metal carbonyl hydrides, such as $H_3Mn_3(CO)_{12}$ and $HRe_2Mn(CO)_{14}$, the mass spectra of which possessed fragments due to consecutive loss of CO as well as H; while Edgar et al. (171) studied certain mono- and dinuclear metal carbonyl halides, such as $Mn(CO)_5X$ and $Re_2(CO)_8Cl_2$, as well as some sulphur-bridged compounds such as $Fe_2(CO)_6S_2R_2$. The latter authors were able to show that the mononuclear derivatives lost both CO and X at the same time, whereas the X- or S-bridged binuclear compounds lost CO before losing X or S. The mass spectrum can therefore be used to distinguish between bridging and terminal X or S groups.

Mass spectroscopic studies have also been used to determine metal-metal bond dissociation energies, thus Bidinosti and McIntyre were able to obtain values of 18.9 ± 1.4 kcal. for the Mn-Mn bond dissociation energy in $Mn_2(CO)_{10}$ (138), and 11.5 ± 4.6 for the Co-Co bond in $Co_2(CO)_8$ (172).

RESULTS AND DISCUSSION

In the present work, mass spectra were employed mainly as an aid in the characterization of compounds. This involved the identification of the observed ions from their mass numbers and a knowledge of the elements present. This identification was made simpler when a polyisotopic element was present in the compound, as ions containing it could be identified by the appearance of the isotope pattern characteristic of that element. Thus, when tin is present, a pattern similar to that shown in Figure 53 is seen. In this figure the relative abundance of an isotope is plotted against its mass number (its atomic mass given to the nearest whole number). In practice, the mass numbers of the observed fragments will be given by the sum of each of the tin isotope mass numbers and the mass numbers of all the other atoms present. If more than one polyisotopic element is present, the situation is more complicated, and it is necessary to calculate the expected pattern. This is done by combining each isotope of one element with each of the isotopes of the other, and calculating both the relative abundance and the mass for each combination. The relative abundances of all combinations with the same mass number are then added together, and the results plotted in the same way as in Figure 53. The results of such a calculation are shown in Figure 54 for an SnBr fragment.

The mass spectra of $\text{Me}_3\text{SnCo}(\text{CO})_4$, $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$ and $\text{MeSn}[\text{Co}(\text{CO})_4]_3$ are reported in detail in Tables XII to XIV, and the mass spectra of $\text{R}_3\text{SnCo}(\text{CO})_4$ and $\text{RSn}[\text{Co}(\text{CO})_4]_3$ are summarized in Table XV in which the fragments observed are reported. From these results it is seen that fragments corresponding to consecutive loss of both CO molecules, and cobalt atoms were observed.

The mass spectra of $\text{R}_3\text{SnCo}(\text{CO})_4$ possessed fragments corresponding to $\text{R}_3\text{SnCo}(\text{CO})_x^+$ as well as fragments due to loss of R groups. The latter fragments were more pronounced in $\text{Me}_3\text{SnCo}(\text{CO})_4$ (where $\text{Me}_2\text{SnCo}(\text{CO})_x^+$, MeSnCo^+ and SnCo^+ appeared in medium abundance (see Table XII)), than they were in $\text{Cl}_3\text{SnCo}(\text{CO})_4$.

The mass spectrum of $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$ possessed fragments due to $\text{Cl}_2\text{SnCo}_2(\text{CO})_x^+$ where $x = 0-7$, but the molecular ion ($x = 8$) could not be seen. No carbonyl containing fragments in which sn-Cl bond fission had occurred were observed.

The predominating fragments observed in the mass spectra of both $\text{XSn}[\text{Co}(\text{CO})_4]_3$ and $\text{RSn}[\text{Co}(\text{CO})_4]_3$ belonged to the series $\text{RSnCo}_3(\text{CO})_x^+$ produced by consecutive loss of CO from the molecular ion, $\text{RSnCo}_3(\text{CO})_{12}^+$. Only in the case of the methyl, phenyl and fluoro derivatives, however, was this parent ion actually observed, and even then in low abundance. In all cases the ion $\text{RSnCo}_3(\text{CO})_{11}^+$ was present in moderate to high

TABLE XII

Mass Spectrum of $\text{Me}_3\text{SnCo(CO)}_4$

Ion	m/e ^a	% \sum_{59}^b	Ion	m/e	% \sum_{59}
$\text{Me}_3\text{SnCo(CO)}_4^+$	336	3.90	SnCo(CO)^+	207	3.45
$\text{Me}_2\text{SnCo(CO)}_4^+$	321	1.18	MeSnCo^+	194	17.24
$\text{Me}_3\text{SnCo(CO)}_3^+$	308	6.17	SnCo^+	179	6.53
$\text{Me}_2\text{SnCo(CO)}_3^+$	293	1.09	Me_3Sn^+	165	9.62
$\text{Me}_3\text{SnCo(CO)}_2^+$	280	6.71	Me_2Sn^+	150	1.45
$\text{Me}_2\text{SnCo(CO)}_2^+$	265	2.27	Co(CO)_3^+	142	0.27
$\text{Me}_3\text{SnCo(CO)}^+$	252	3.45	MeSn^+	135	3.81
$\text{Me}_2\text{SnCo(CO)}^+$	237	2.45	Sn^+	120	1.81
Me_3SnCo^+	224	2.90	Co(CO)_2^+	115	3.08
MeSnCo(CO)^+	222	3.27	Co(CO)^+	87	4.99
Me_2SnCo^+	209	3.45	Co^+	59	2.722

^a m/e values for ^{120}Sn -containing fragments.

^b % \sum_{59} = abundance of fragment expressed as a percentage of the sum of all ^{120}Sn - and ^{59}Co - containing fragments observed.

TABLE XIII

Mass Spectrum of $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$

Ion	m/e ^a	% \sum_{59}^b	Ion	m/e	% \sum_{59}
$\text{Cl}_2\text{SnCo}_2(\text{CO})_7^+$	504	31.2	SnCo_2^+	238	0.61
$\text{Cl}_2\text{SnCo}_2(\text{CO})_6^+$	476	3.12	ClSnCo^+	214	2.34
$\text{Cl}_2\text{SnCo}_2(\text{CO})_5^+$	448	4.51	Cl_2Sn^+	190	1.21
$\text{Cl}_2\text{SnCo}_2(\text{CO})_4^+$	420	6.94	CoSn^+	179	5.59
$\text{Cl}_2\text{SnCo}_2(\text{CO})_3^+$	392	2.43	ClSn^+	155	3.94
$\text{Cl}_2\text{SnCo}_2(\text{CO})_2^+$	364	6.59	Sn^+	120	2.25
$\text{Cl}_2\text{SnCo}_2(\text{CO})^+$	336	11.01	$\text{Co}_2^+(\text{}^{118}\text{Sn}^+)$	118	4.03
$\text{Cl}_2\text{SnCo}_2^+$	308	7.19	$\text{Co}(\text{CO})_2^+$	115	6.33
$\text{Cl}_2\text{SnCo}(\text{CO})_2^+$	305	4.59	$\text{Co}(\text{CO})^+$	87	9.71
$\text{Cl}_2\text{SnCo}(\text{CO})^+$	277	3.29	Co^+	59	8.84
Cl_2SnCo^+	249	2.34			

^a m/e values for ^{120}Sn -containing fragments.

^b % \sum_{59} = abundance of fragment expressed as a percentage of all observed ^{120}Sn - and ^{59}Co -containing fragments.

TABLE XIV

Mass Spectrum of $\text{MeSn}[\text{Co}(\text{CO})_4]_3$

Ion	x ^a	m/e ^b	% \sum_{59}^c	Ion	x	m/e	% \sum_{59}
$\text{MeSnCo}_3(\text{CO})_x^+$	12	648	0.07		8	521	0.28
	11	620	2.38		7	493	0.14
	10	592	0.61		6	465	1.36
	9	564	0.14		5	437	1.19
	8	536	0.54		4	409	0.25
	7	508	2.93		3	381	0.28
	6	480	6.13		2	353	0.68
	5	452	7.28		1	325	0.78
	4	424	5.04		0	297	5.14
	3	396	6.26	$\text{MeSnCo}_2(\text{CO})_x^+$	8	477	1.67
	2	368	5.17		5 ^d	393	4.77
	1	340	5.58		4 ^d	365	0.85
	0	312	6.13		3 ^d	337	1.83
$\text{SnCo}_3(\text{CO})_x^+$	12	633	0.07		2 ^d	309	0.66
	11	605	0.12		1	281	1.84
	10	577	0.03		0	253	2.01
	9	549	0.40				

TABLE XIV (continued)

Ion	x ^a	m/e ^b	% \sum_{59}^c	Ion	x	m/e	% \sum_{59}^c
SnCo ₂ (CO) _x ⁺	1	266	0.33		3	143	0.7
	0	238	5.45		2	115	3.06
MeSnCo(CO) ⁺	-	222	0.19		1	87	4.50
SnCo ⁺	-	179	2.72		0	59	4.00
Co(CO) _x ⁺	4	171	0.17	Co ₂ ⁺	-	118	2.25

^a Value of x for series shown in left-hand column.

^b m/e values for ¹²⁰Sn-containing fragment.

^c % \sum_{59}^c = abundance of fragment expressed as a percentage of all ¹²⁰Sn- and ⁵⁹Co-containing fragments.

^d Superimposed on MeSnCo₃(CO)_x⁺.

TABLE XV

Summary of Mass Spectra ^a

Ion	$\frac{R_3\text{SnCo(CO)}_4}{x}$			
	$R_3 = \text{Me}_3$	Ph_2Cl	PhCl_2	Cl_3
$R_3\text{SnCo(CO)}_x^+$	0-4	0-3	0-3	0,1,3,4
$R_2\text{SnCo(CO)}_x^+$	0-4	$0^b, 0^c$	$0^c, 0, 1^d$	0
RSnCo(CO)_x^+	0,1	-	0^e	0
SnCo(CO)_x^+	0,1	-	-	0
Co(CO)_x^+	0-3	0-2	0-3	0-4

Ion	$\frac{\text{RSn[Co(CO)}_4\text{]}_3}{x}$						
	R=Me	Vn^f	Ph	F	Cl	Br	I
$\text{RSnCo}_3(\text{CO})_x^+$	0-12	0-11	0-12	0-12	0-11	0-11	0-11
$\text{RSnCo}_2(\text{CO})_x^+$	0-5,8	0-5,7,8	0-5,8	0-8	0-6,8	0-8	0-6
RSnCo(CO)_x^+	1,2	0,2	0,1	0,1	0	0,1	-
$\text{SnCo}_3(\text{CO})_x^+$	0-12	0	0,12	-	-	-	-
SnCo(CO)_x^+	0,1	2,3	3,5	0	0	0	-
SnCo(CO)_x^+	0	0,2-4	0	0	0	0	-
Co(CO)_x^+	0-4	0-4	0-4	0-3	0-4	0-4	-
Co_2^+	g	g	g	g	g	g	g

^a Entries in the tables indicate values of x for which fragments were observed; m-n indicates that all values of x from m to n were observed, and m,n indicates that intermediate fragments could not be identified.

^b $R_2 = \text{Ph}_2$ ^c $R_2 = \text{PhCl}$ ^d $R_2 = \text{Cl}_2$ ^e $R = \text{Cl}$

^f $\text{Vn} = \text{CH}_2\text{:CH-}$ ^g Fragment observed

abundance compared to the other fragments. This is illustrated in Figures 55 and 56 where the relative abundance expressed as a percentage of all the observed fragments, is plotted against the number of CO groups present in $\text{RSnCo}_3(\text{CO})_x^+$. This absence of molecular ion was also observed for $\text{Cl}_2\text{PhSnCo}(\text{CO})_4$, $\text{ClPh}_2\text{SnCo}(\text{CO})_4$, $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$, and $\text{Sn}[\text{Co}(\text{CO})_4]_4$, and so appears to be of fairly common occurrence for tetracarbonylcobalt derivatives, a fact which has to be borne in mind when using mass spectra to characterize such compounds.

The next most abundant fragments in nearly all of the tris(tetracarbonylcobalt) derivatives were produced by loss of $\text{Co}(\text{CO})_4$ groups from the molecular ion giving rise to the $\text{RSnCo}_2(\text{CO})_x^+$ series. In most cases the whole series could not be observed owing to overlapping with other more abundant fragments. Also identified in every case were fragments such as Co^+ , $\text{SnCo}(\text{CO})_x^+$, $\text{RSnCo}(\text{CO})_x^+$, $\text{Co}(\text{CO})_x^+$, and Co_2^+ .

The mass spectrum of $\text{Sn}[\text{Co}(\text{CO})_4]_4$ showed the same general features as the other derivatives discussed above. The main fragments observed were $\text{SnCo}_4(\text{CO})_x^+$ where $x = 0$ to 15, and $\text{SnCo}_3(\text{CO})_x^+$ where $x = 0$ to 12.

EXPERIMENTAL

Infrared spectra were recorded using a Perkin-Elmer Grating Infrared Spectrophotometer fitted with a very slow scan motor (72 minutes to scan the 4000 to 1200 cm^{-1} range). The output was used to drive a Texas Instruments Servo-Riter II external recorder, with variable chart speed. For calibration purposes the chart speed was adjusted to 3 in./min. so that 100 cm^{-1} was spread over 19.1 cm. of chart. With the sample and reference cell in position the recorder and spectrophotometer were started, the latter scanning from about 2170 cm^{-1} . A carbon monoxide cell was held in the sample beam so that the spectrum of CO was recorded on the chart paper. When the central portion of the spectrum had been recorded (including band number 31), the cell was withdrawn and the spectrum of the sample allowed to record itself on the chart. The frequency of the bands could then be determined by measuring the distance from band 31 to the band under investigation, and the corresponding frequency read from a calibration graph. This was prepared by recording the complete spectrum of CO and DBr on the same piece of chart paper, and plotting the distance of each band from band 31 in the CO spectrum against the published frequencies of the bands (173).

All spectra were measured in spectroscopic grade cyclohexane solution at a concentration of 1-2 mg./ml. using sealed 0.5 mm KBr cells.

Mass spectra were obtained with an AEI MS9 double-focusing mass spectrometer operating at 1.5 to 2.2 kV. Solid samples were introduced on the end of a probe and allowed to evaporate near the ionizing electron beam. Because of thermal instability of many of the compounds, the ion source was allowed to cool by turning off the electron beam until immediately before the spectrum was determined. The m/e values of fragments observed were obtained by counting, providing there were fragments at every mass number up to the biggest fragment observed. In the case of tin-containing compounds this was usually the case owing to the large number of isotopes present. If the m/e values could not be determined in this way, the exact mass of the fragment of interest could be measured to 1 ppm. by comparison with a fragment of a reference compound introduced into the mass spectrometer at the same time as the sample.

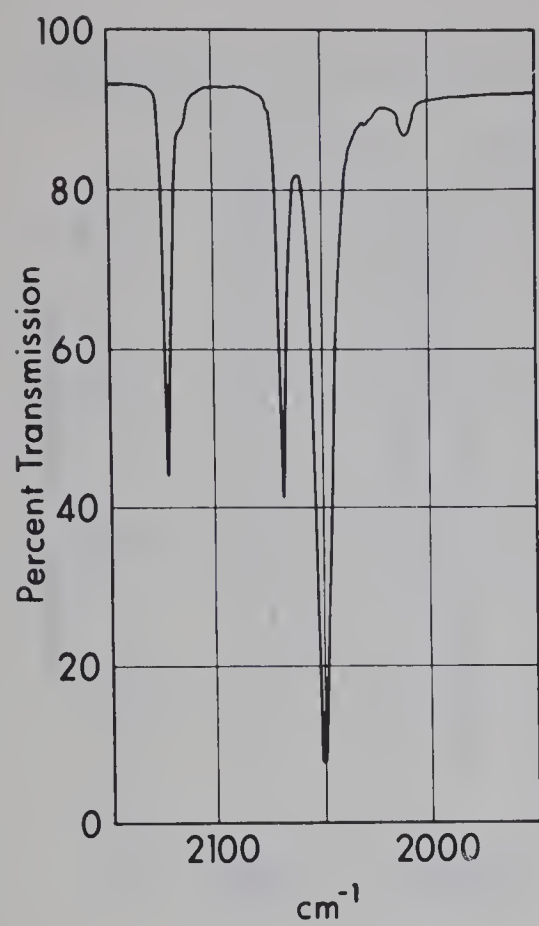


Figure 2

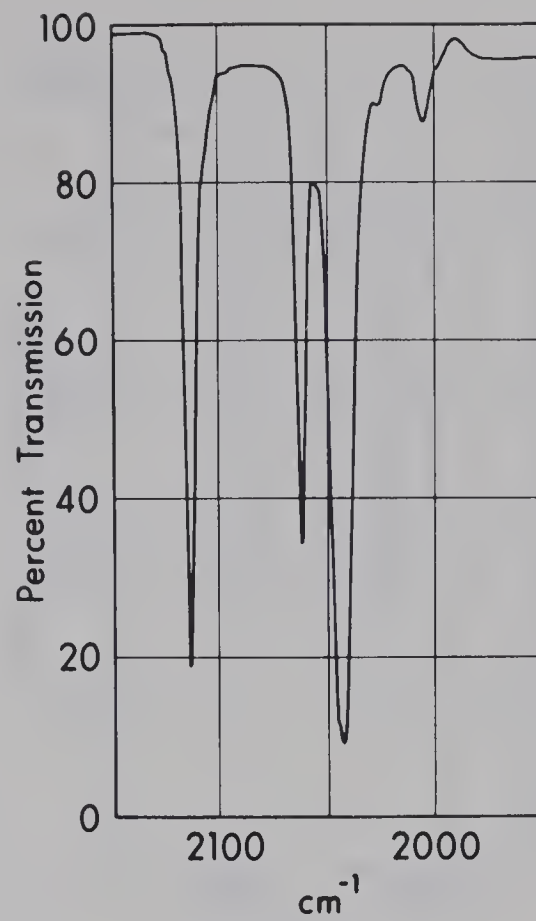


Figure 3

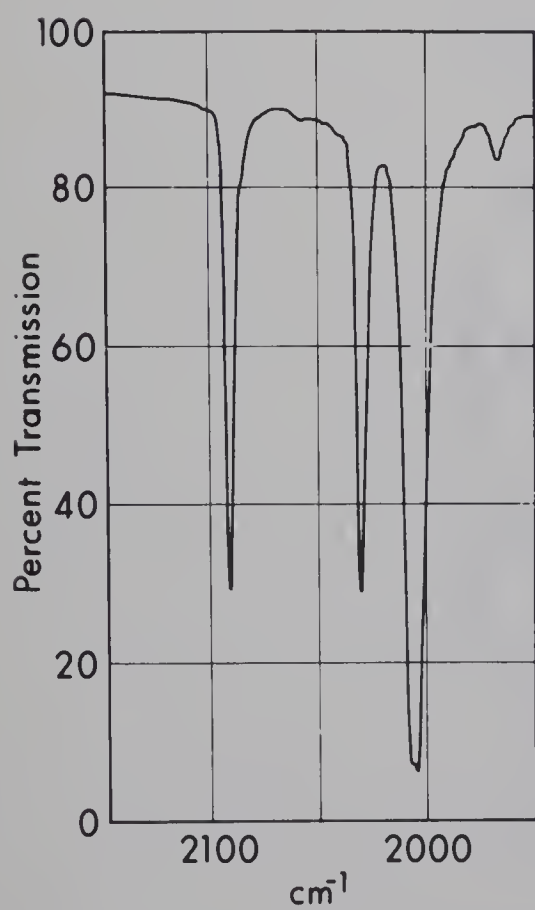


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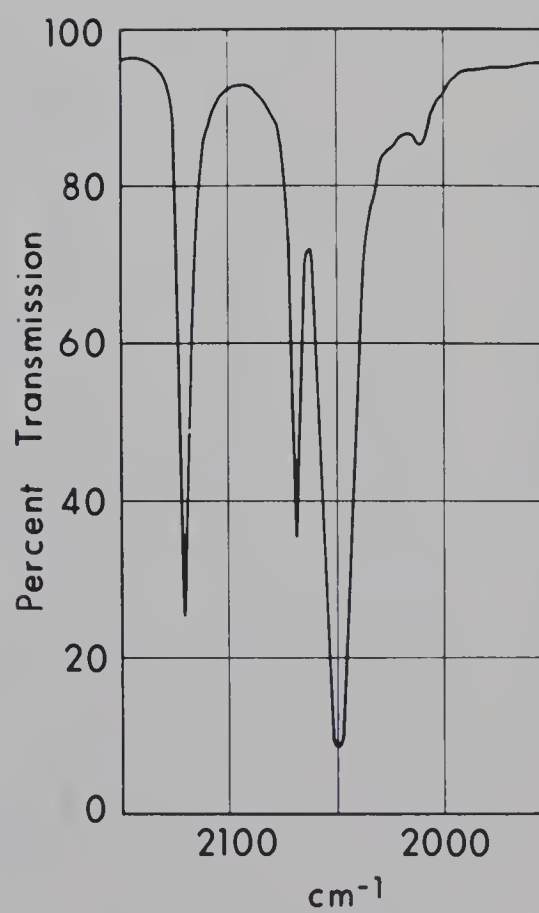
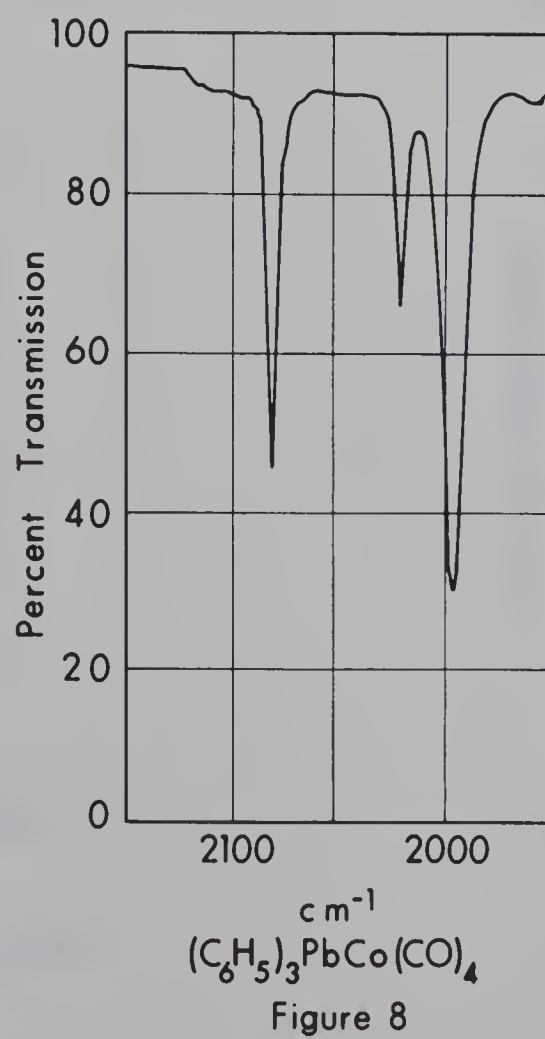
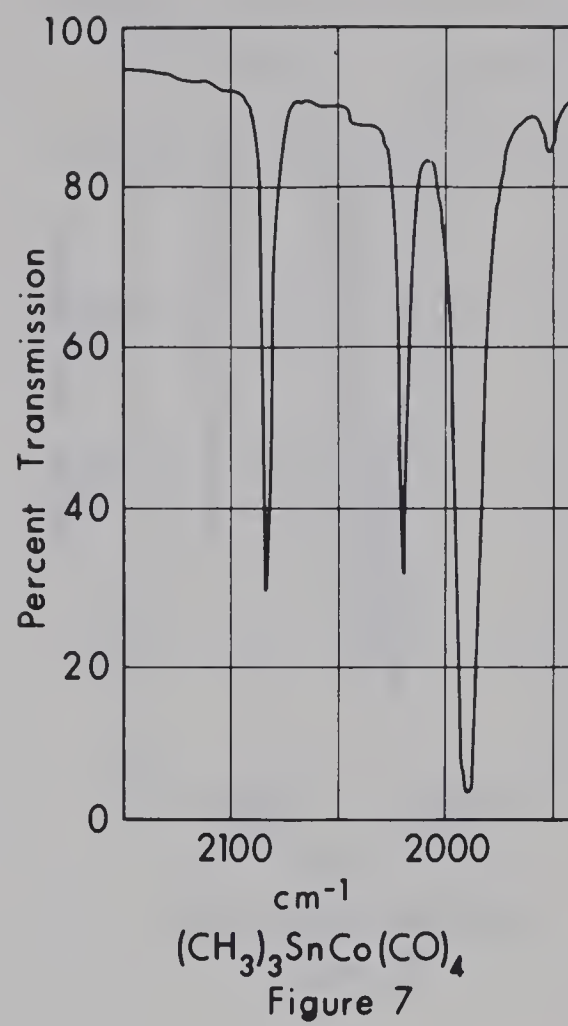
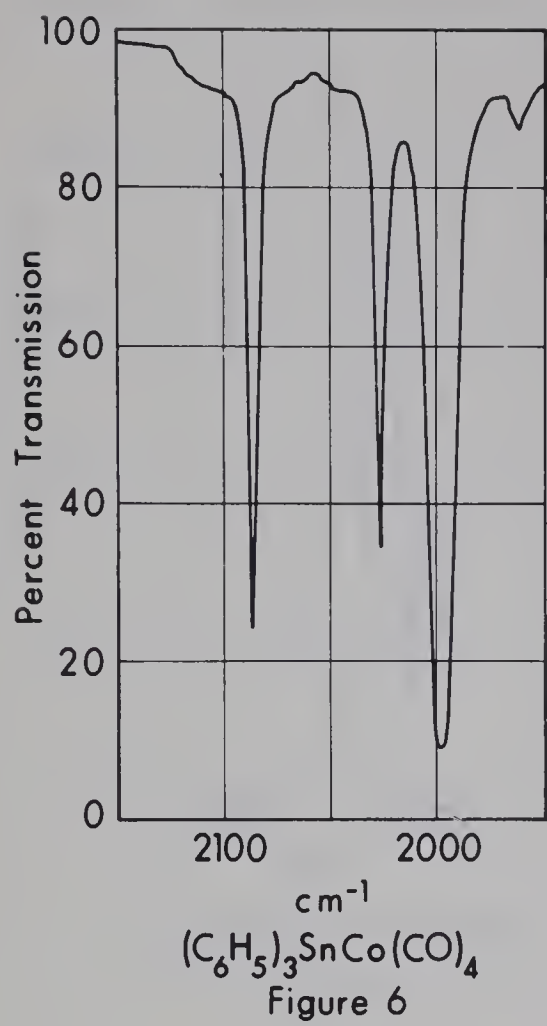


Figure 5



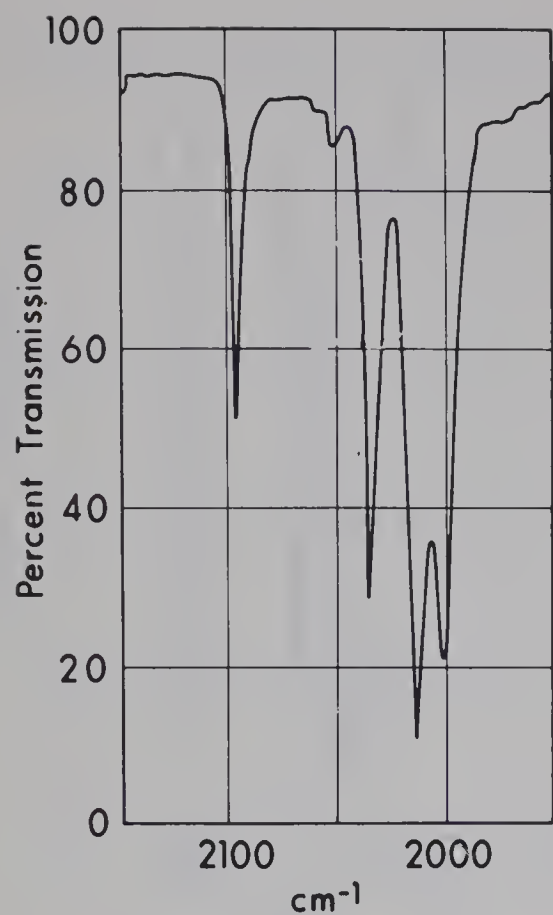


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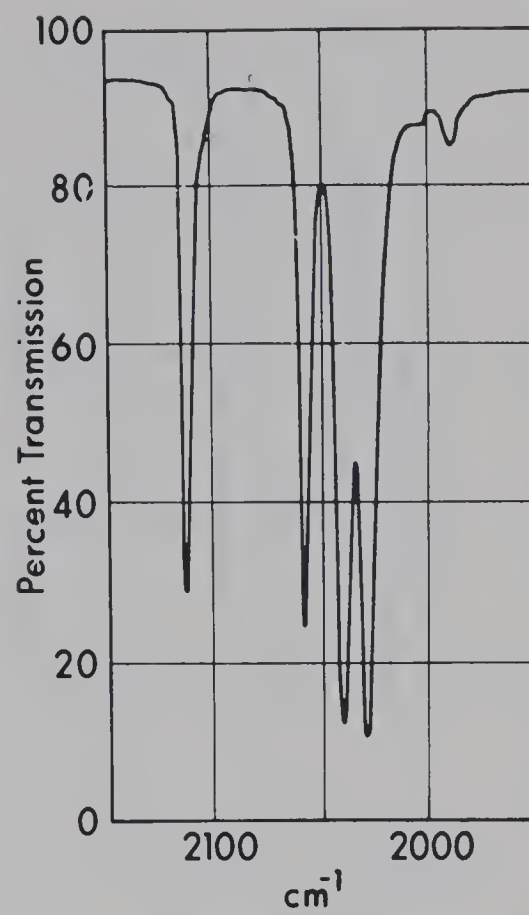


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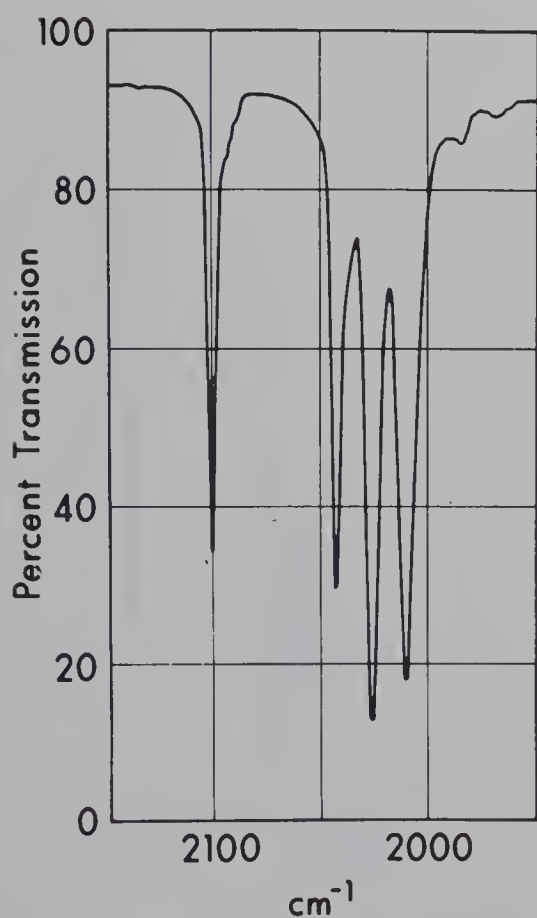


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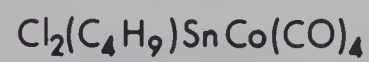
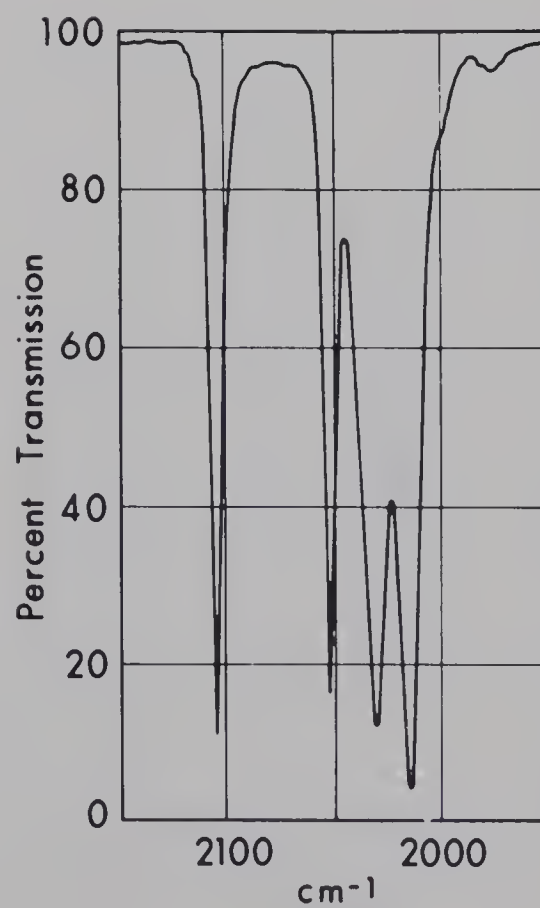


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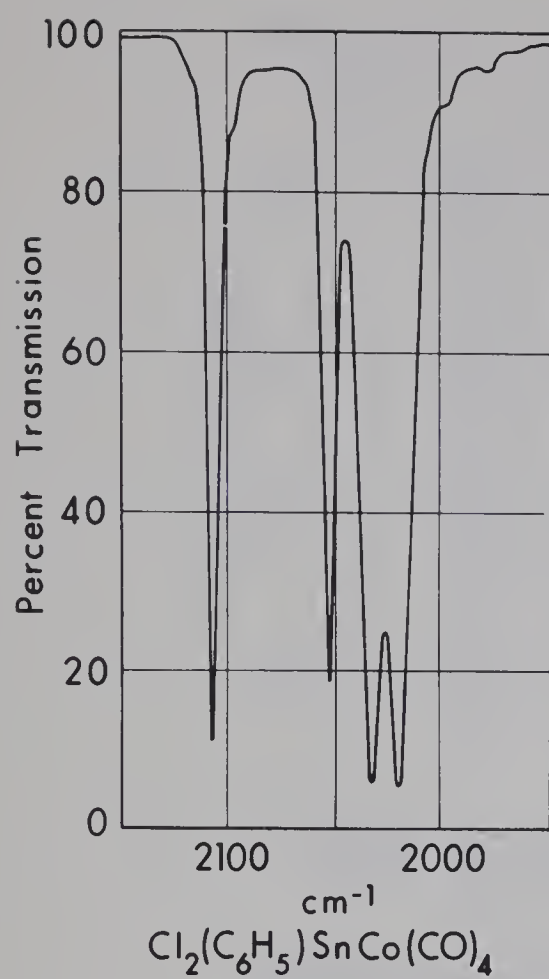


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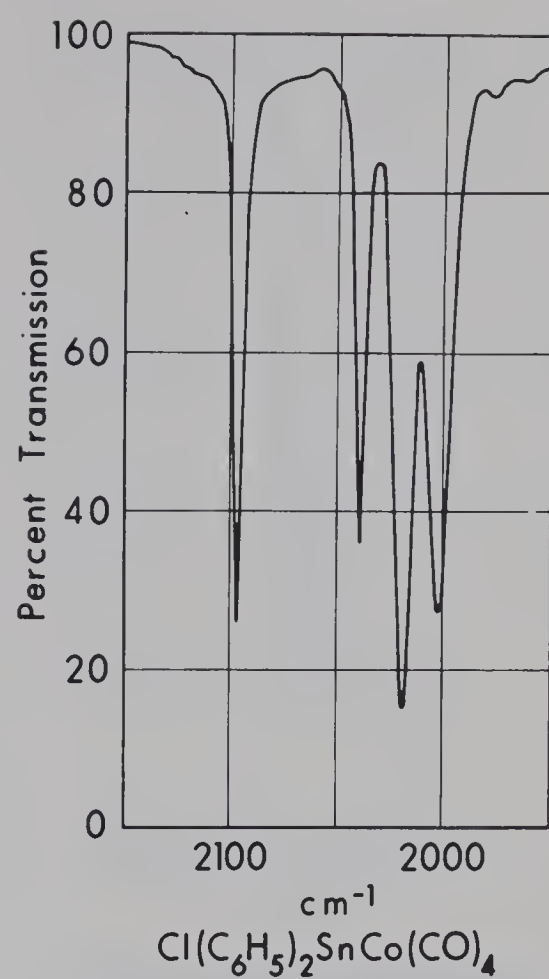


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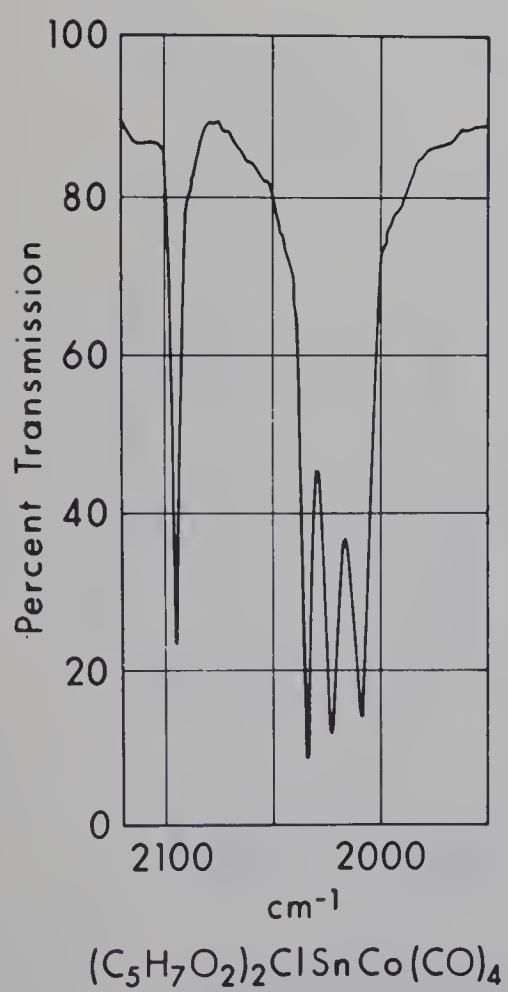


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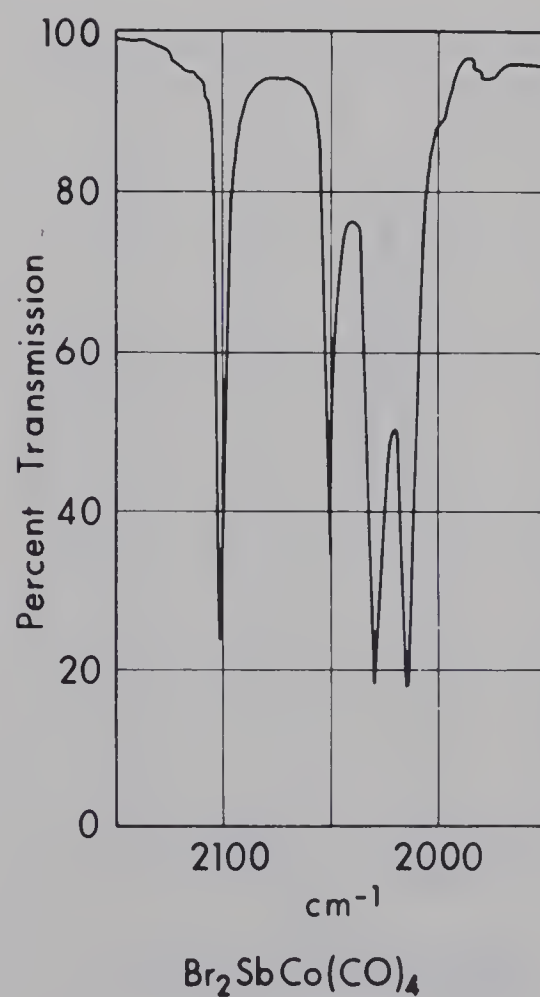


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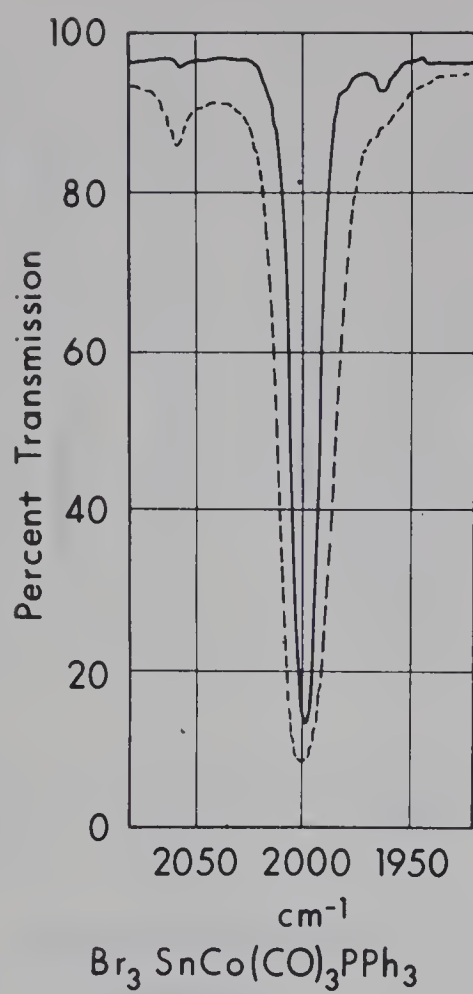


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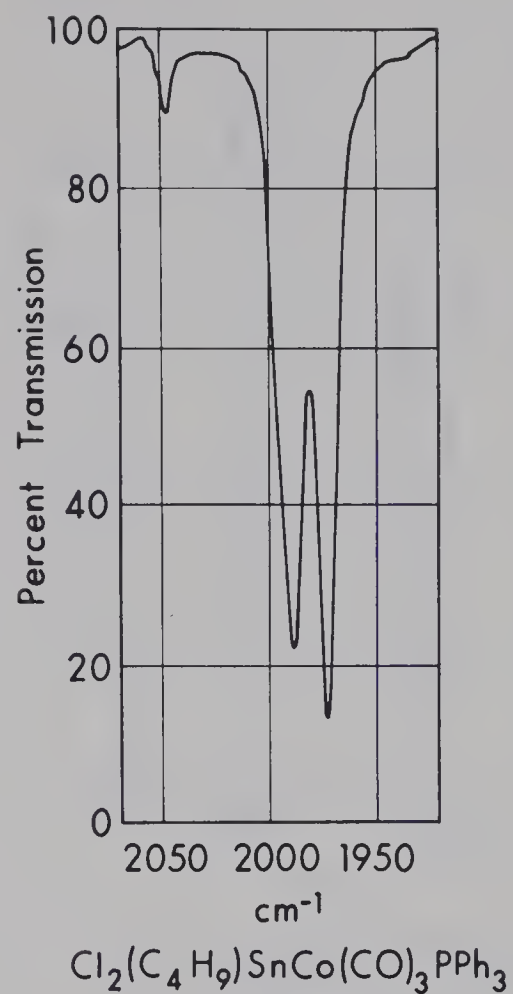


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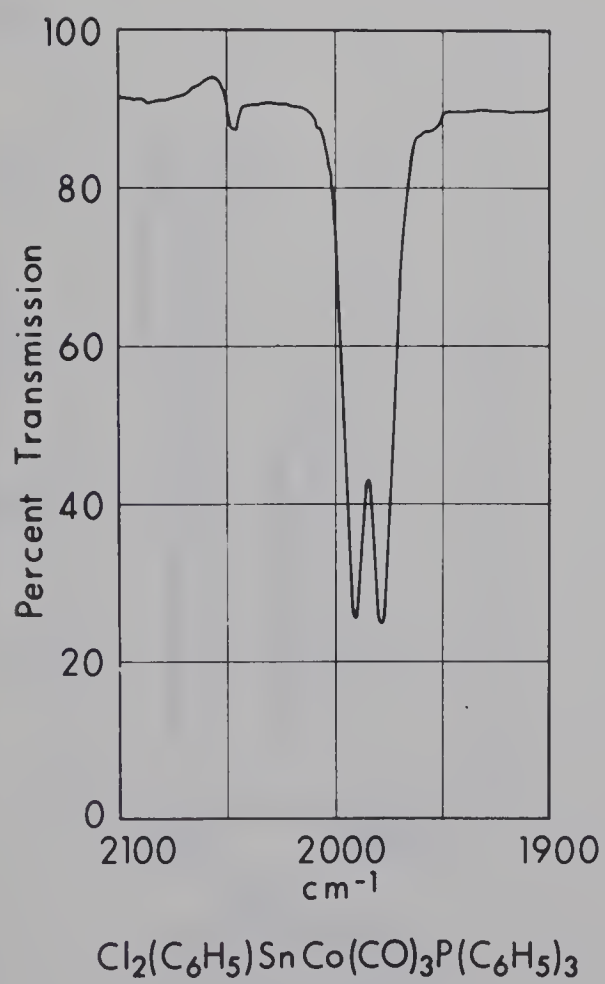


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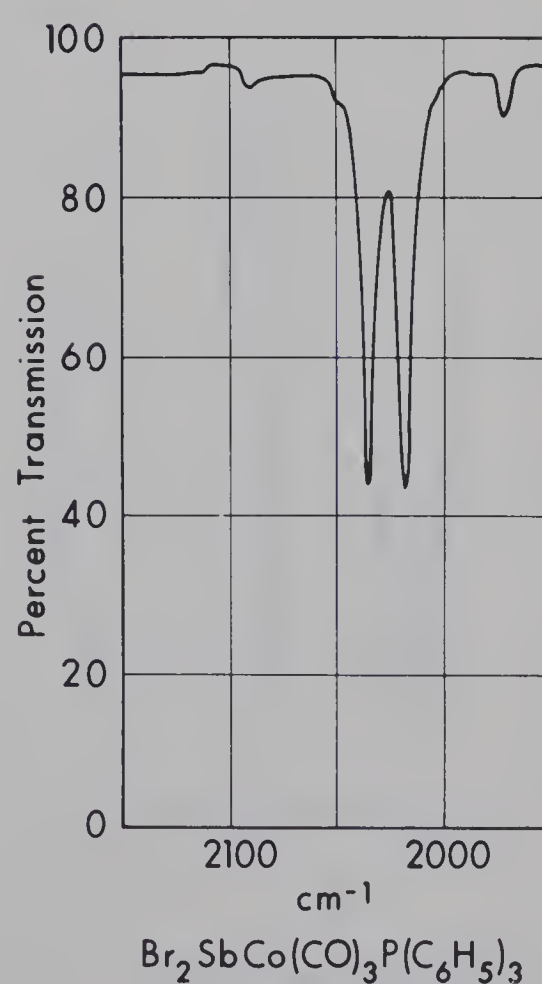
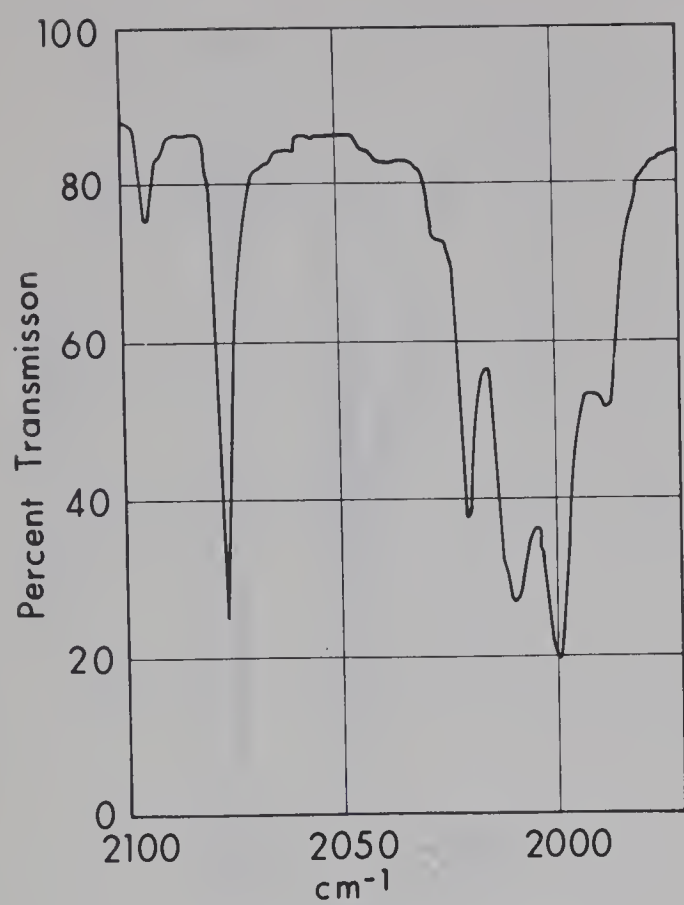
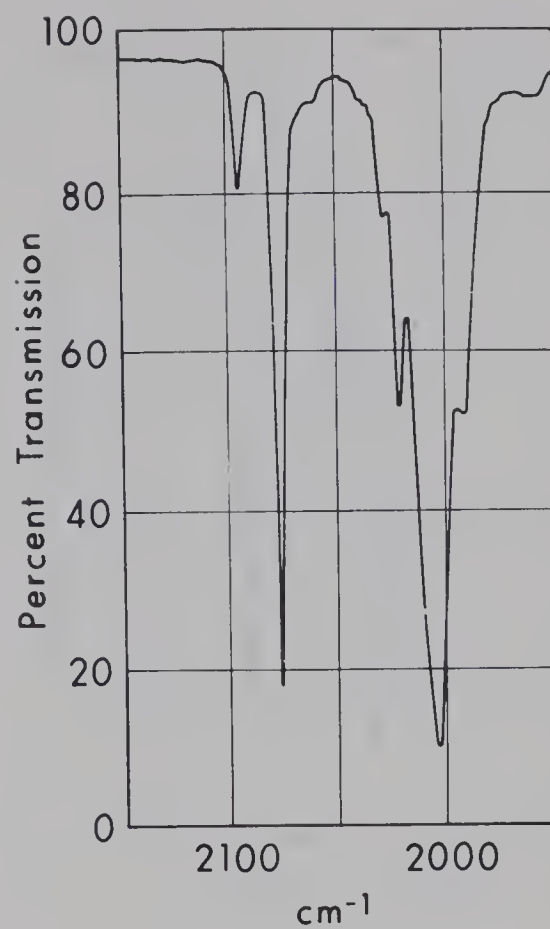


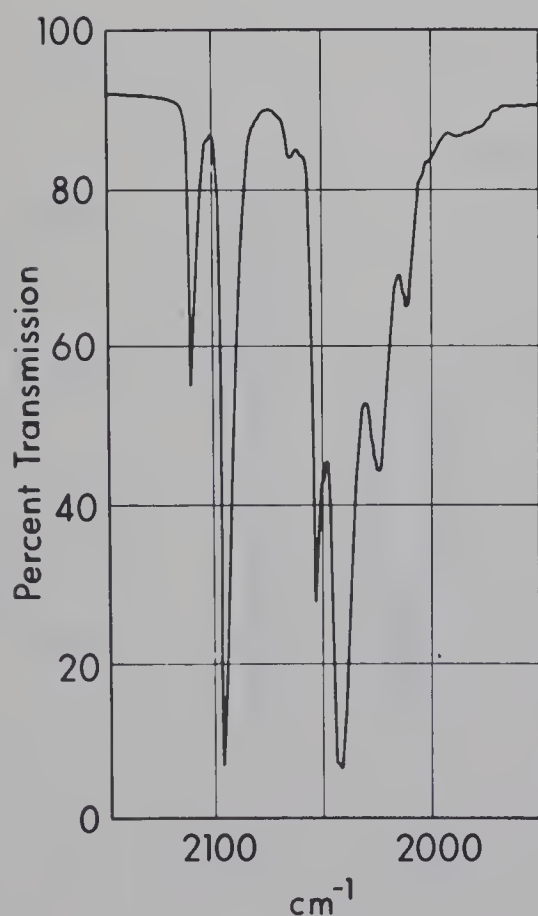
Figure 20



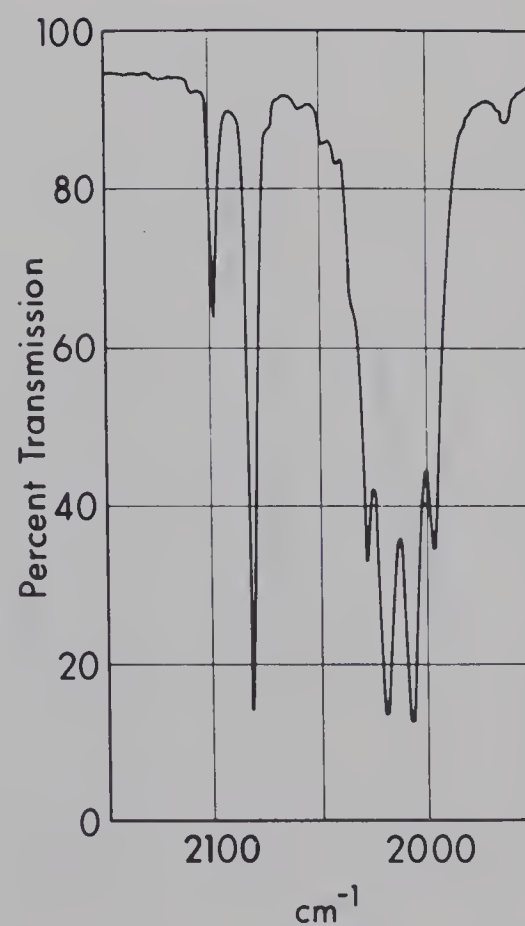
$(C_5H_7O_2)Ga[Co(CO)_4]_2$
Figure 21



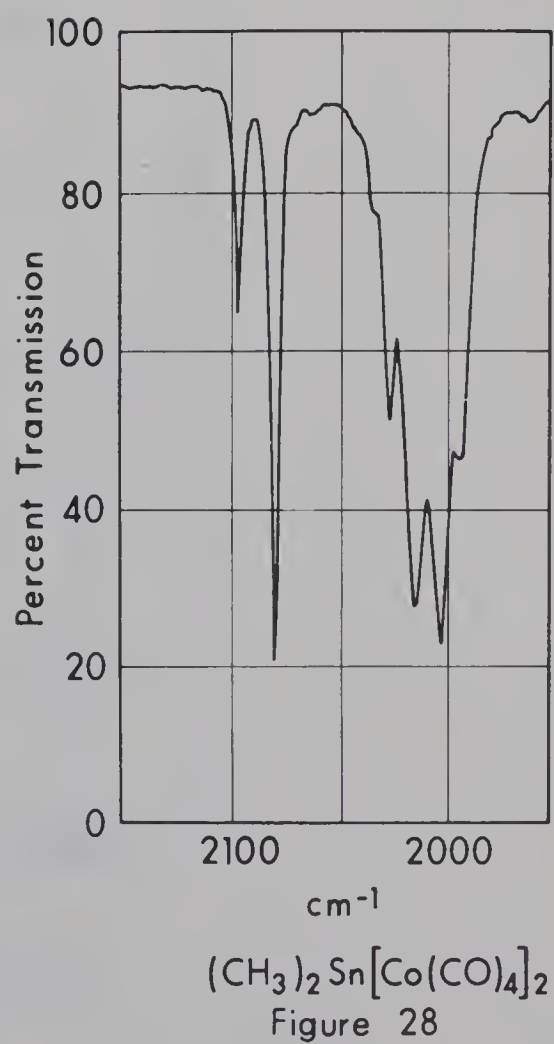
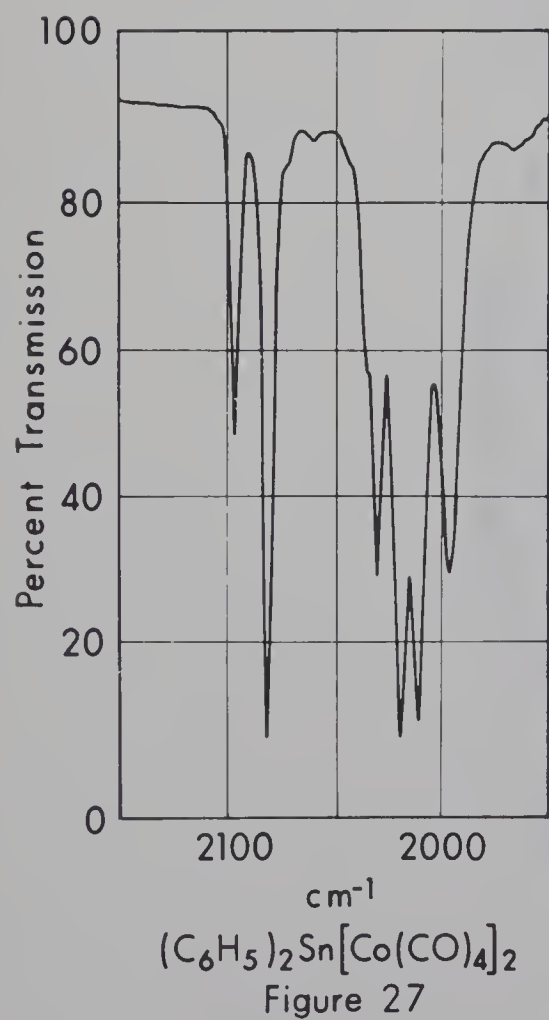
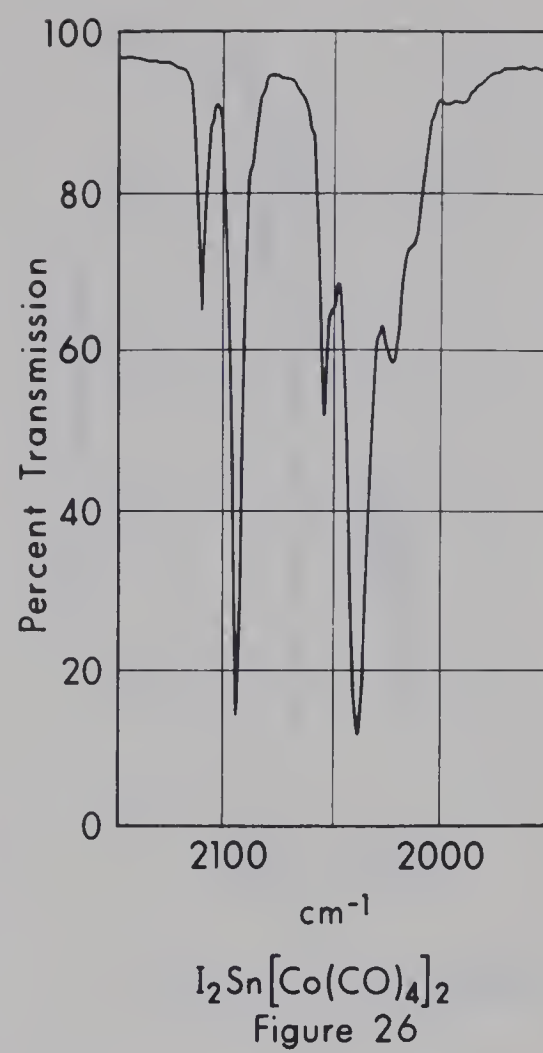
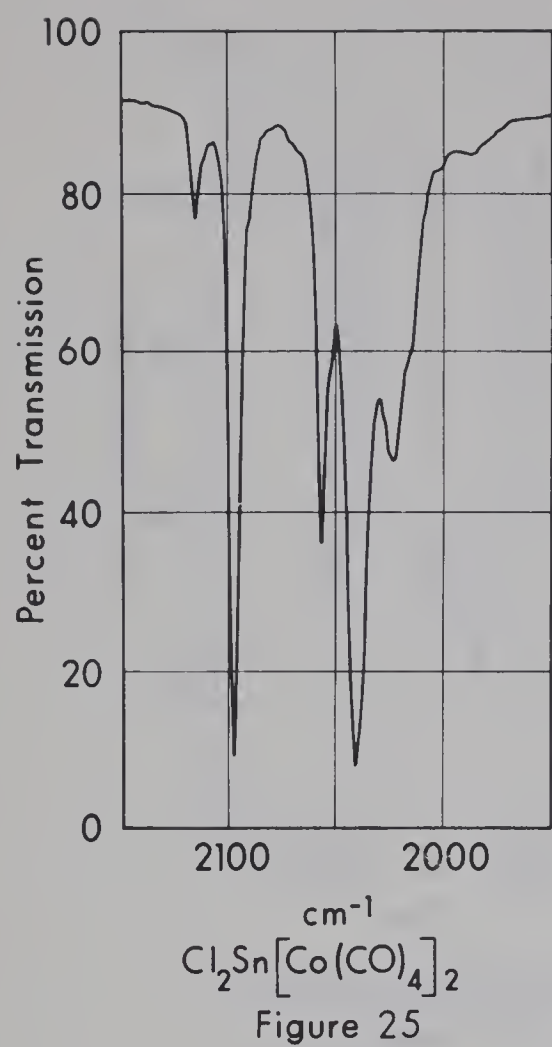
$(C_5H_7O_2)In[Co(CO)_4]_2$
Figure 22

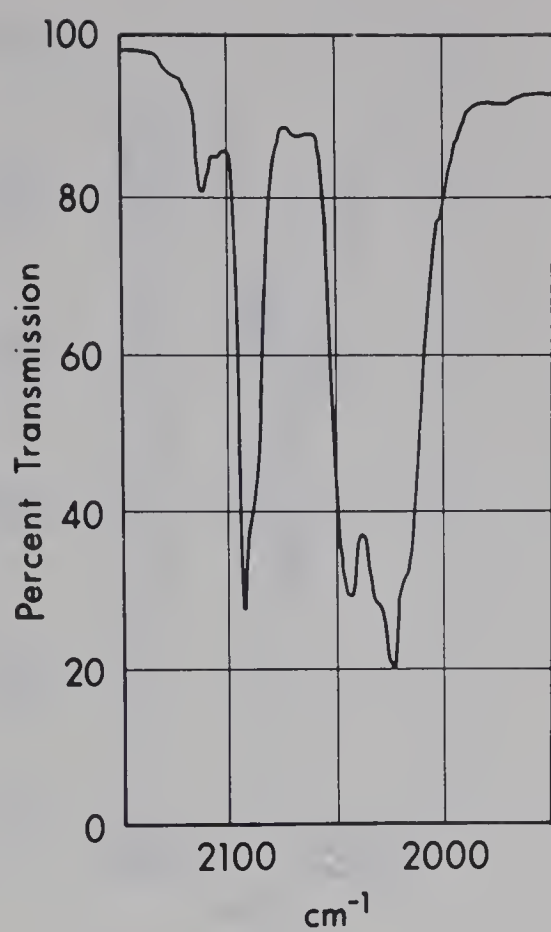


$I_2Ge[Co(CO)_4]_2$
Figure 23

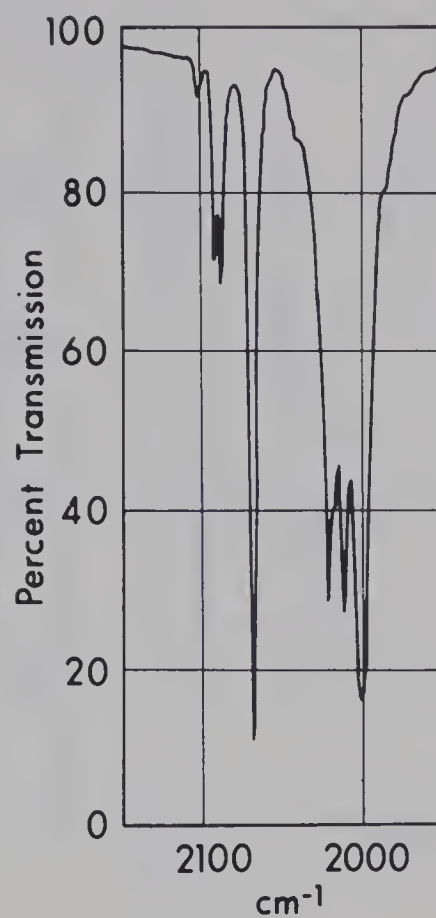


$(CH_3)_2Ge[Co(CO)_4]_2$
Figure 24

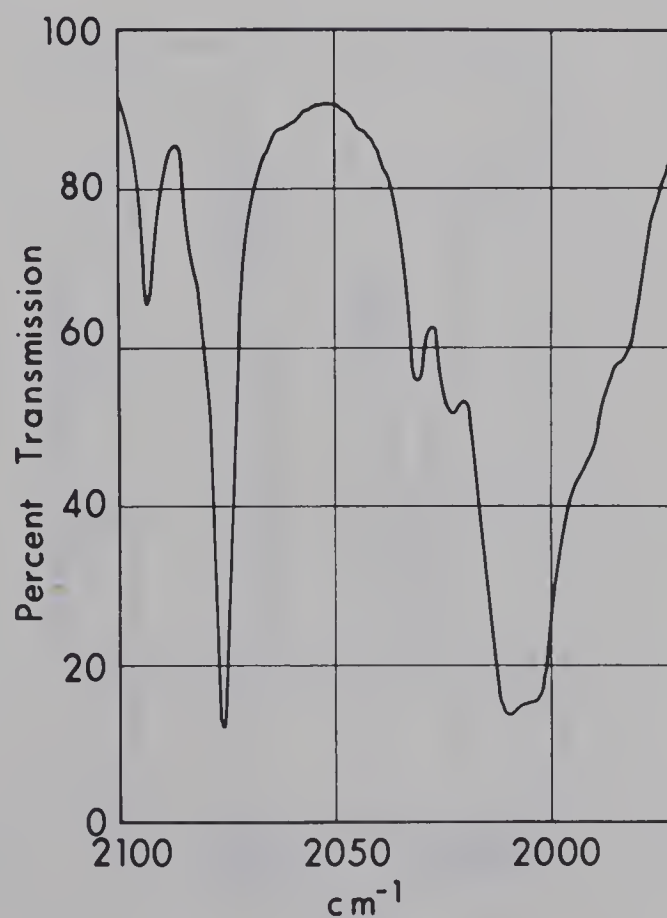




$(\text{CH}_3\text{CO}_2)_2\text{Sn}[\text{Co}(\text{CO})_4]_2$
Figure 29



$(\text{C}_5\text{H}_7\text{O}_2)_2\text{Sn}[\text{Co}(\text{CO})_4]_2$
Figure 30



$\text{BrIn}[\text{Co}(\text{CO})_4]_2 \cdot \text{THF}$
Figure 31

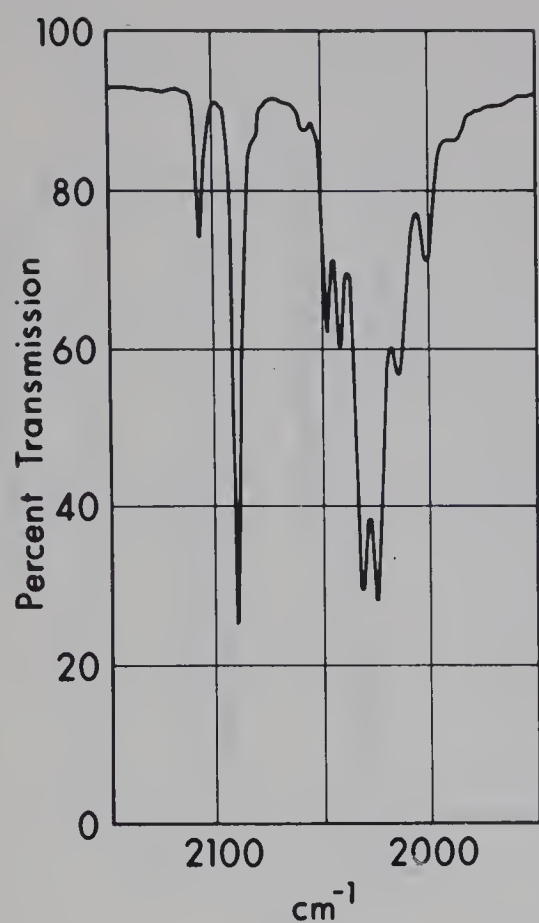


Figure 32

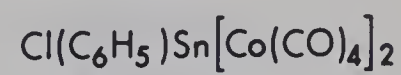
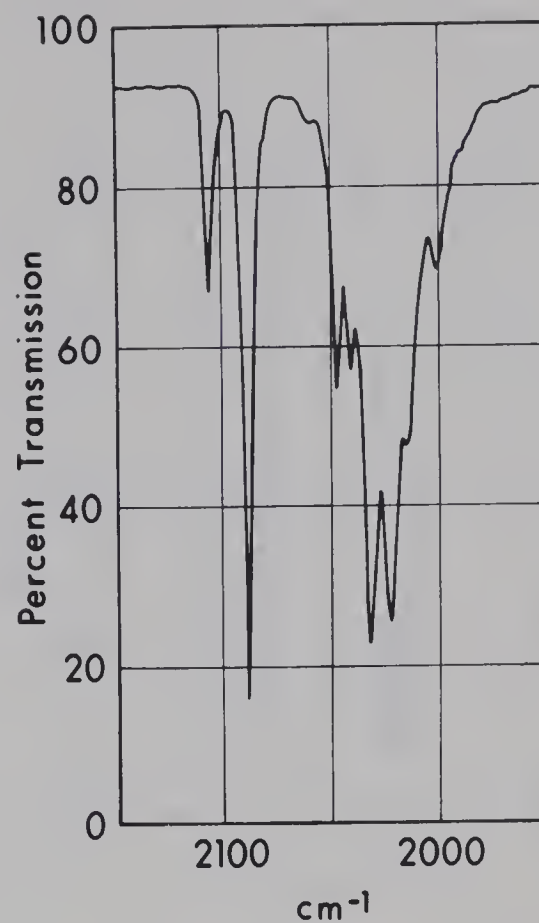


Figure 33

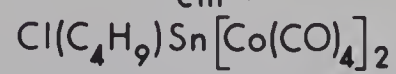
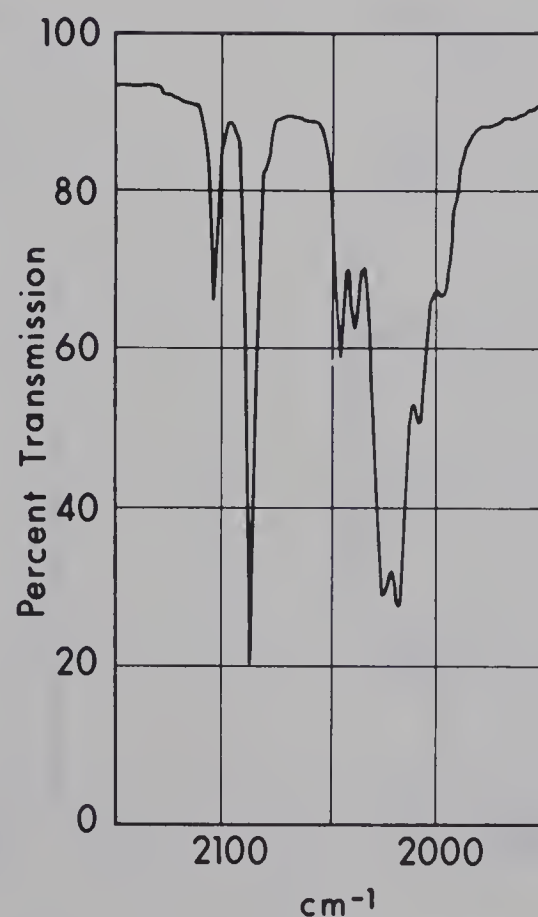
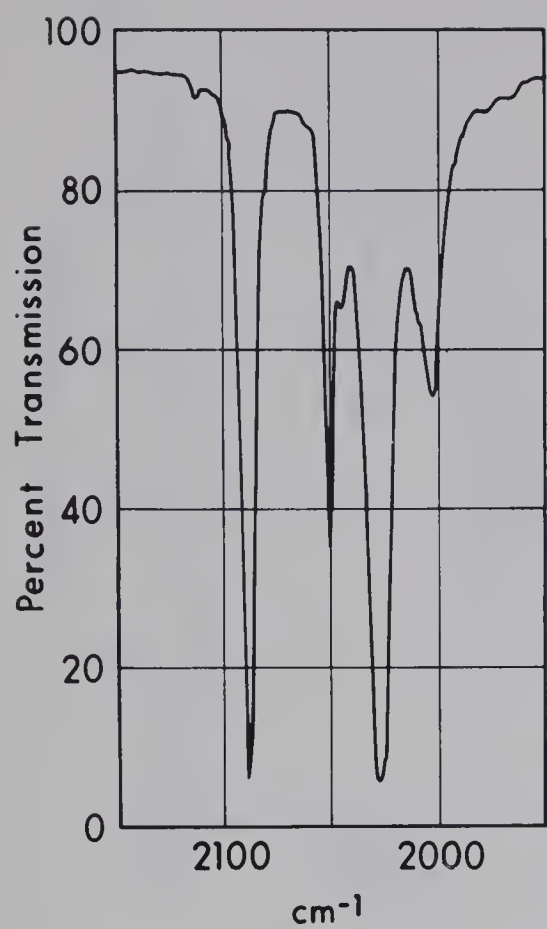
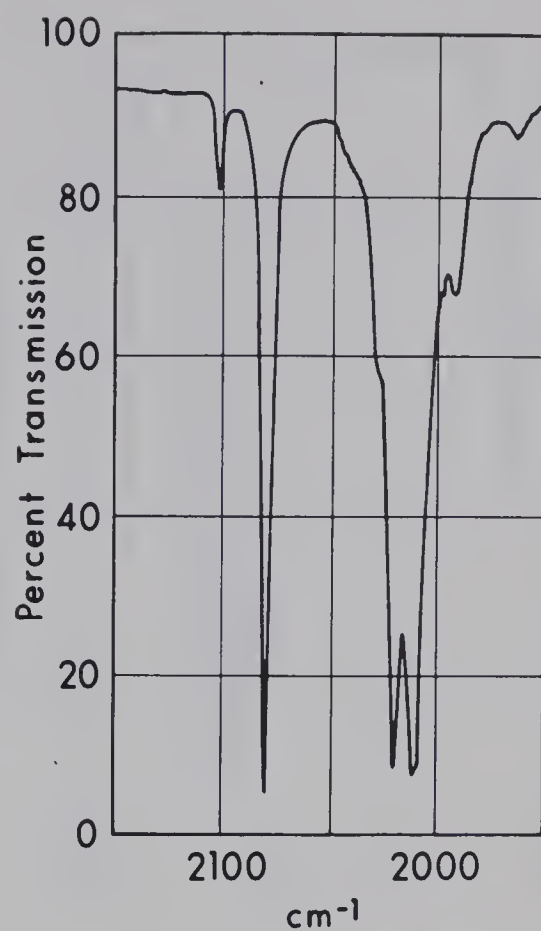


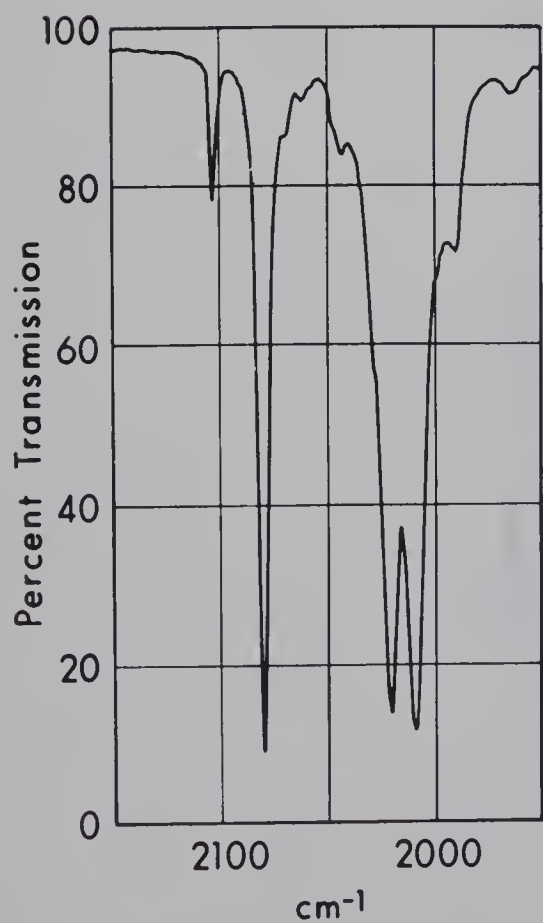
Figure 34



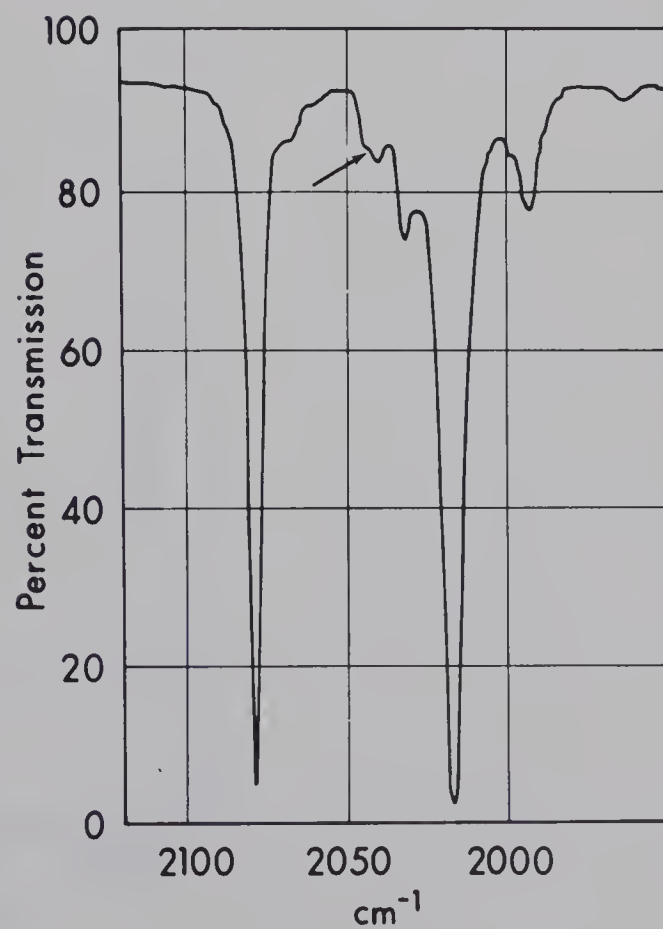
$\text{ClSn}[\text{Co}(\text{CO})_4]_3$
Figure 35



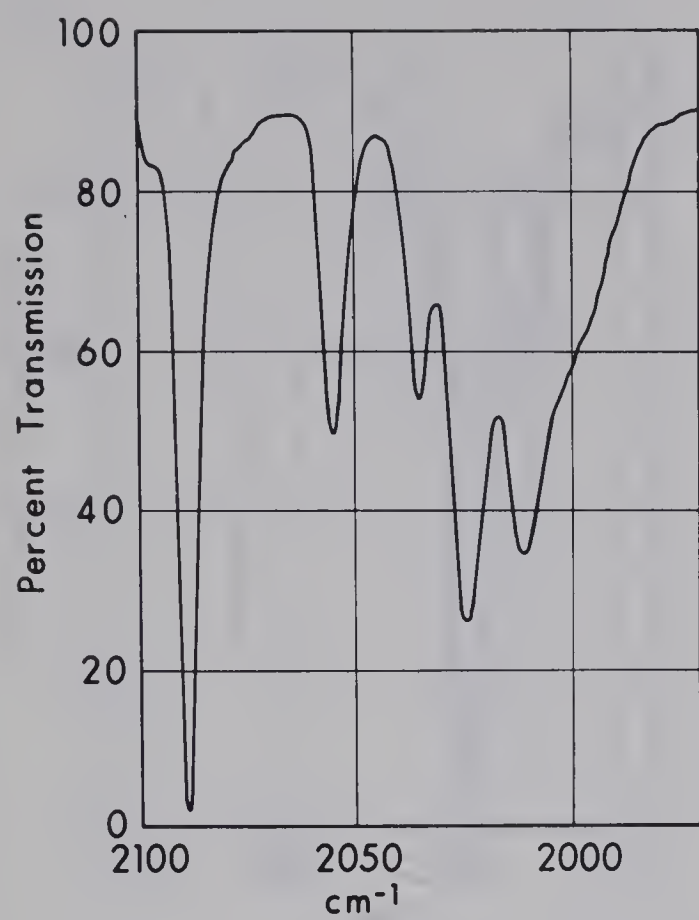
$\text{CH}_3\text{Sn}[\text{Co}(\text{CO})_4]_3$
Figure 36



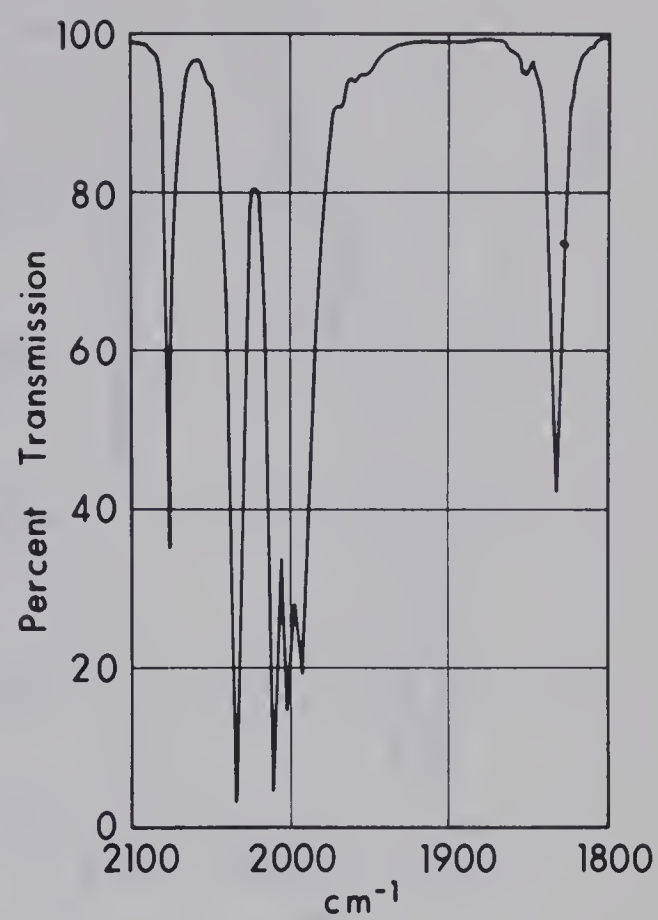
$\text{C}_4\text{H}_9\text{Sn}[\text{Co}(\text{CO})_4]_3$
Figure 37



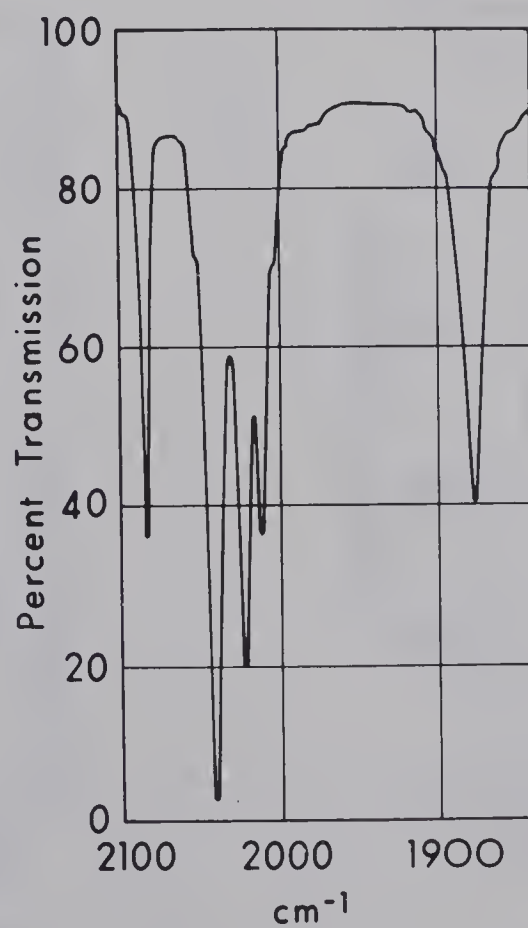
$\text{Sn}[\text{Co}(\text{CO})_4]_4$
Figure 38



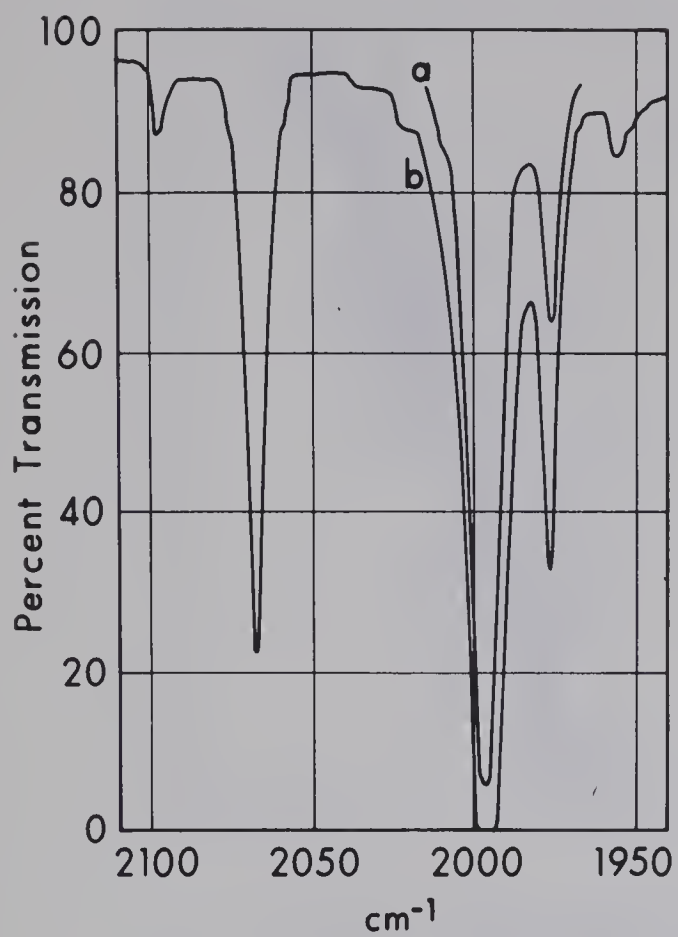
$\text{Br}_3\text{In}_3\text{Co}_4(\text{CO})_{16}$
Figure 39



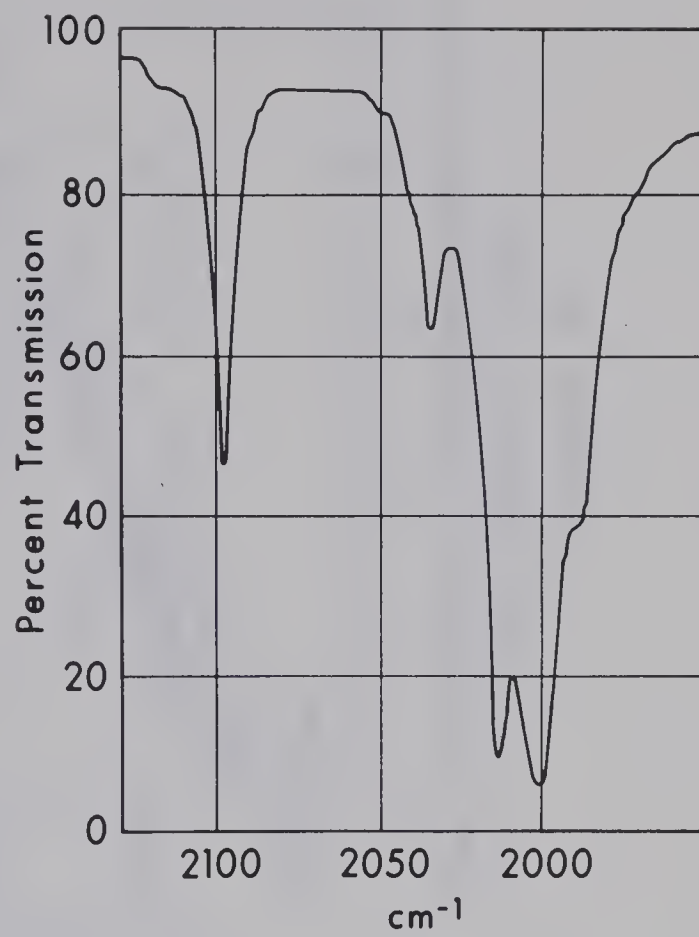
$(\text{C}_5\text{H}_7\text{O}_2)_2\text{SnCo}_2(\text{CO})_7$
Figure 40



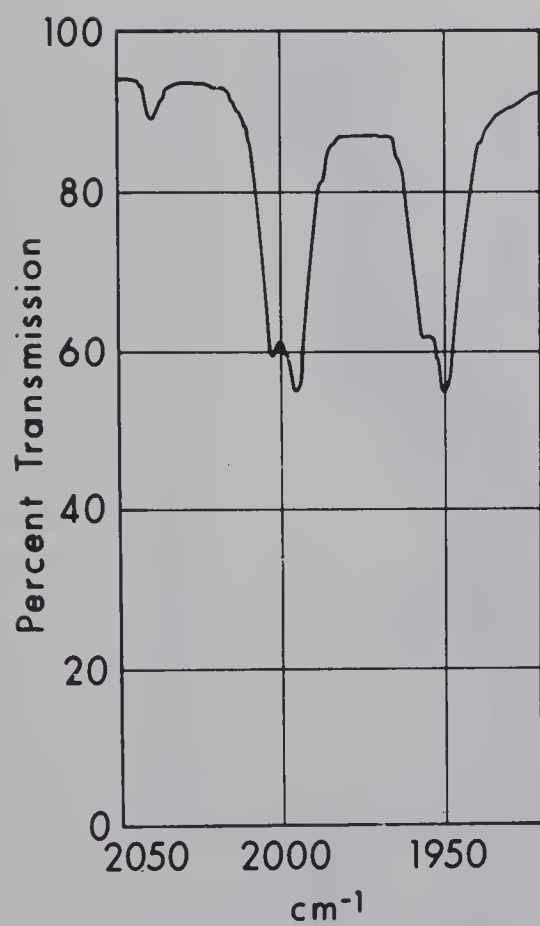
$\text{BiCo}_3(\text{CO})_{10}$
Figure 41



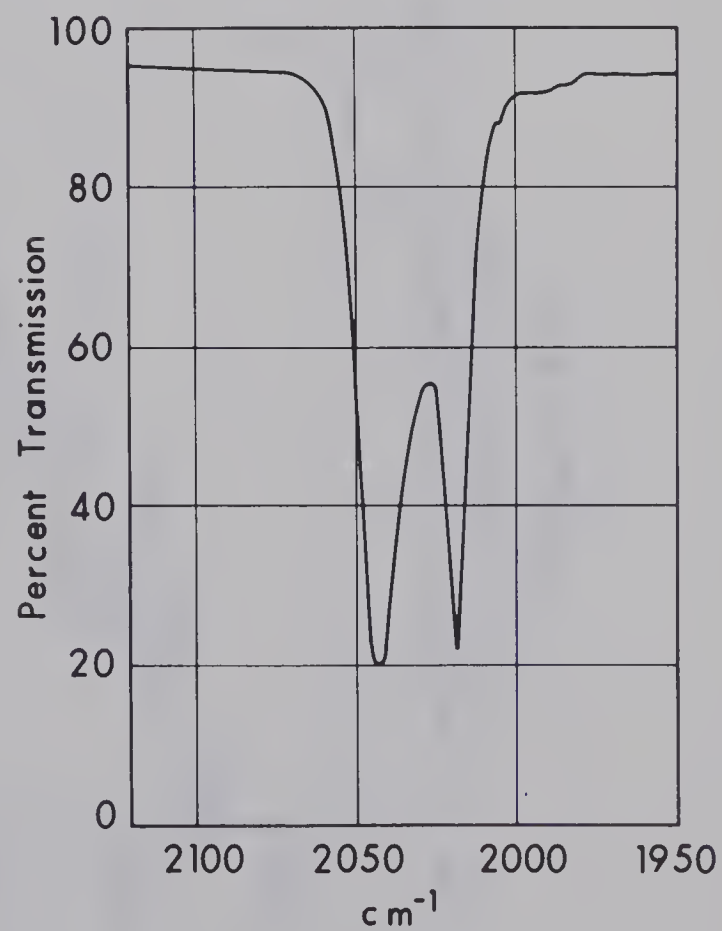
$(C_5H_7O_2)In[Mn(CO)_5]_2$
Figure 42



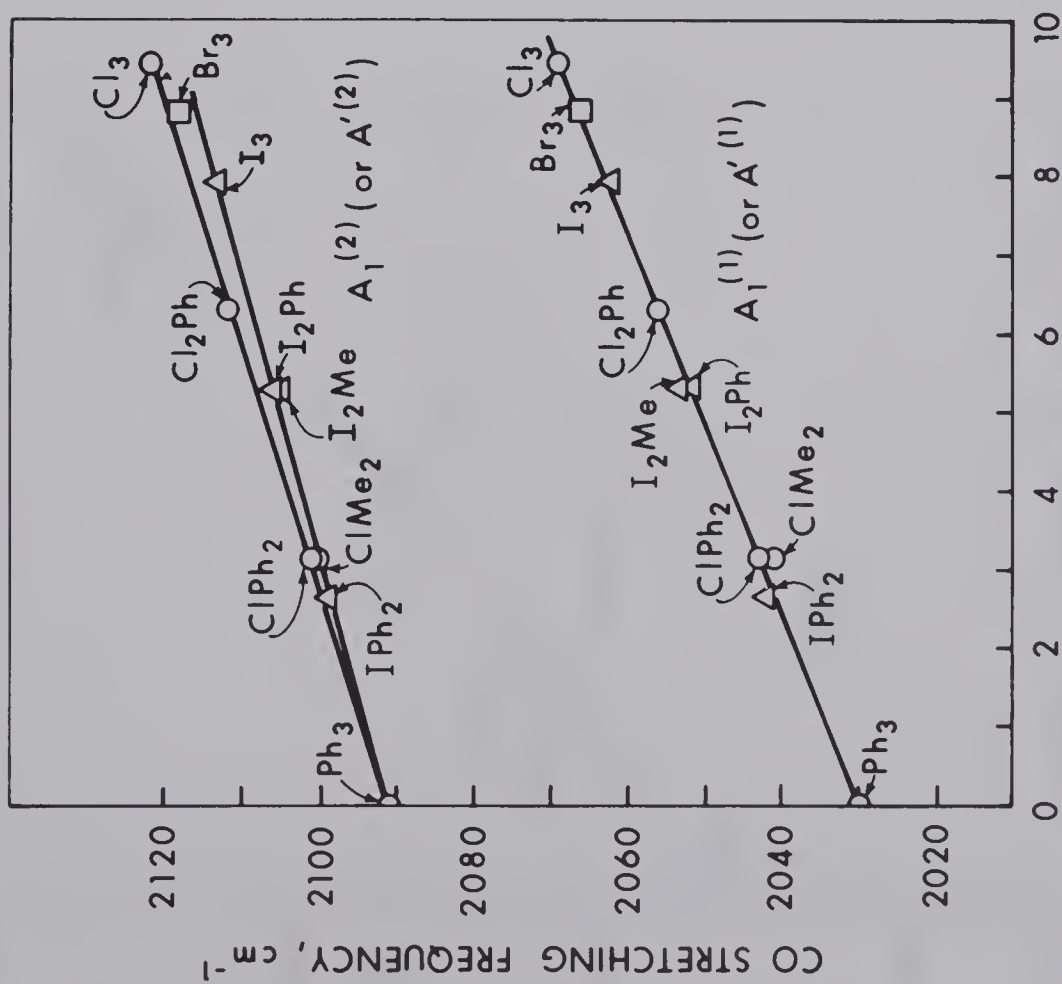
$Br_2InMn(CO)_5$
Figure 43



$I_2InFe(CO)_2\pi C_5H_5 \cdot THF$
Figure 44

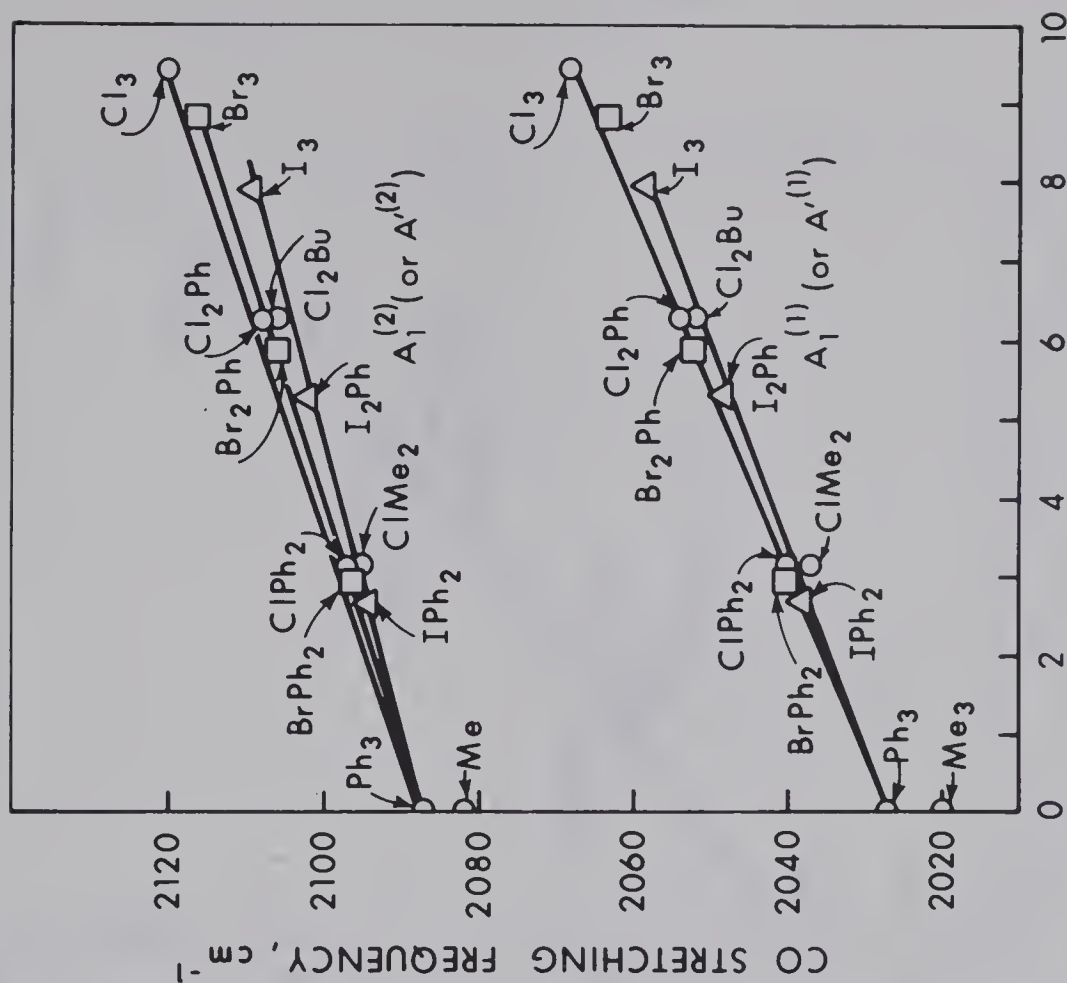


$Cl_2Sn[NiCO(\pi C_5H_5)]_2$
Figure 45



SUM OF HALOGEN ELECTRONEGATIVITIES FOR THE
 $X_nR_{3-n}GeCo(CO)_4$ SERIES

Figure 46



SUM OF HALOGEN ELECTRONEGATIVITIES FOR THE
 $X_nR_{3-n}SnCo(CO)_4$ SERIES

Figure 47

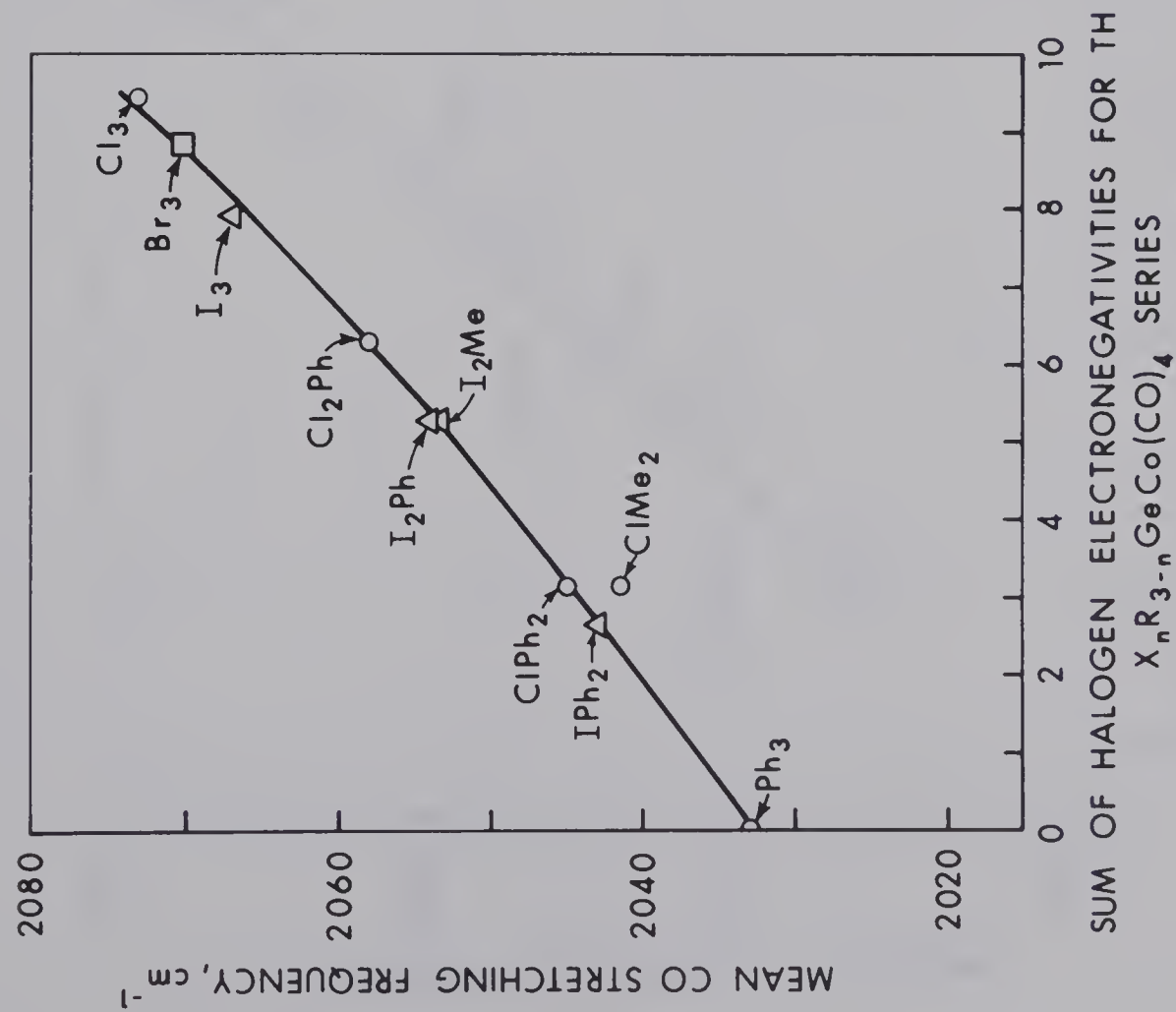


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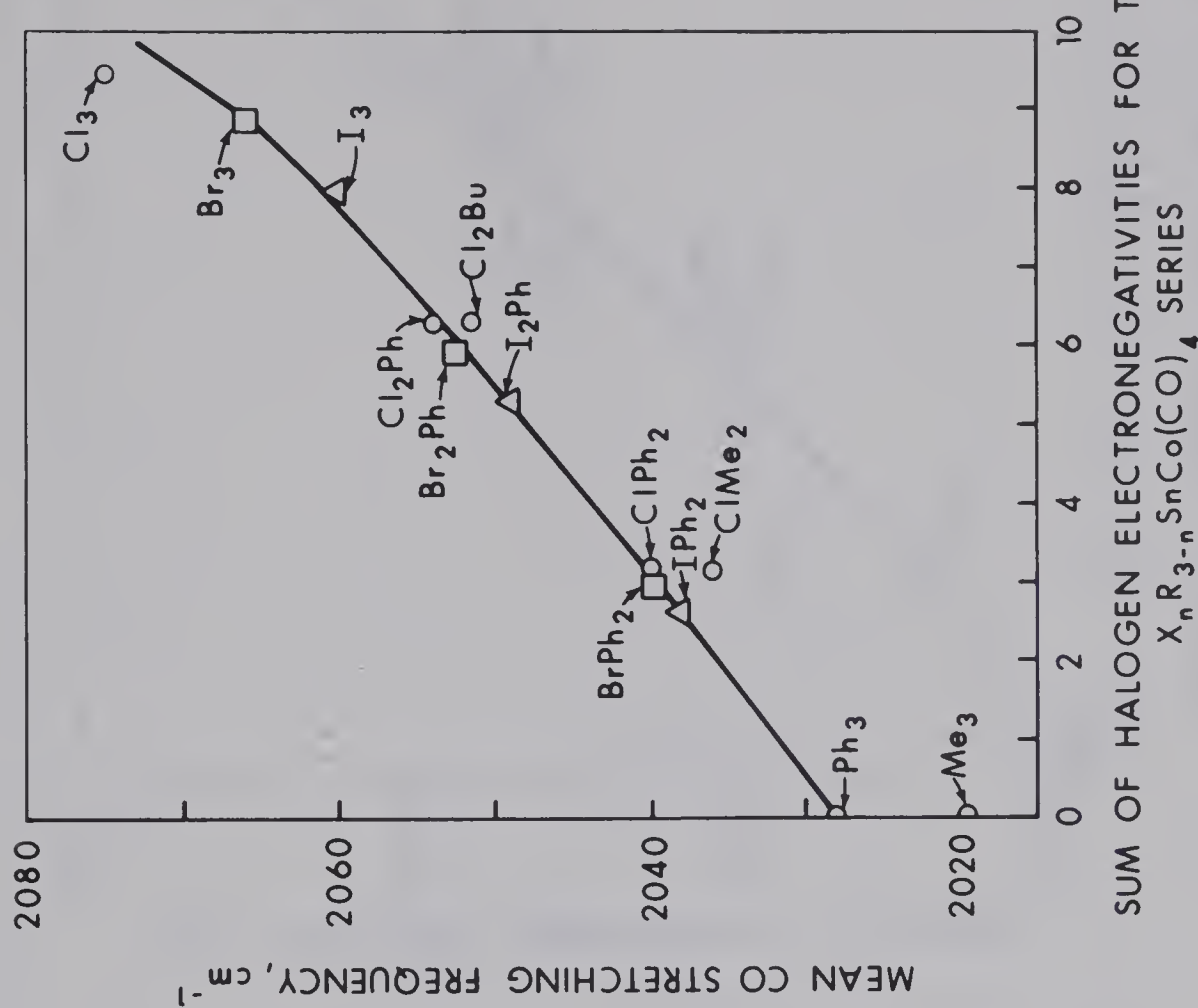


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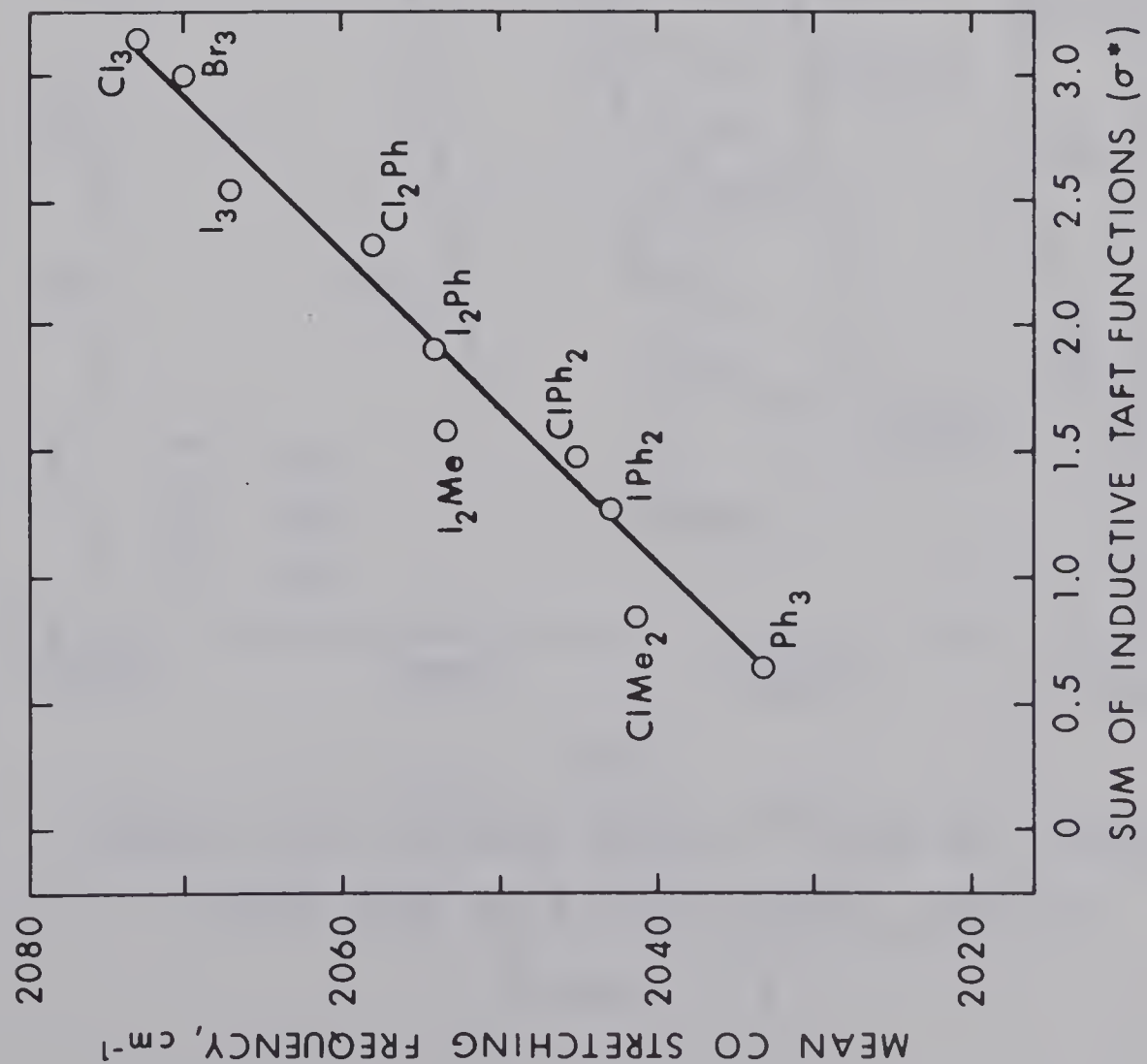


Figure 50

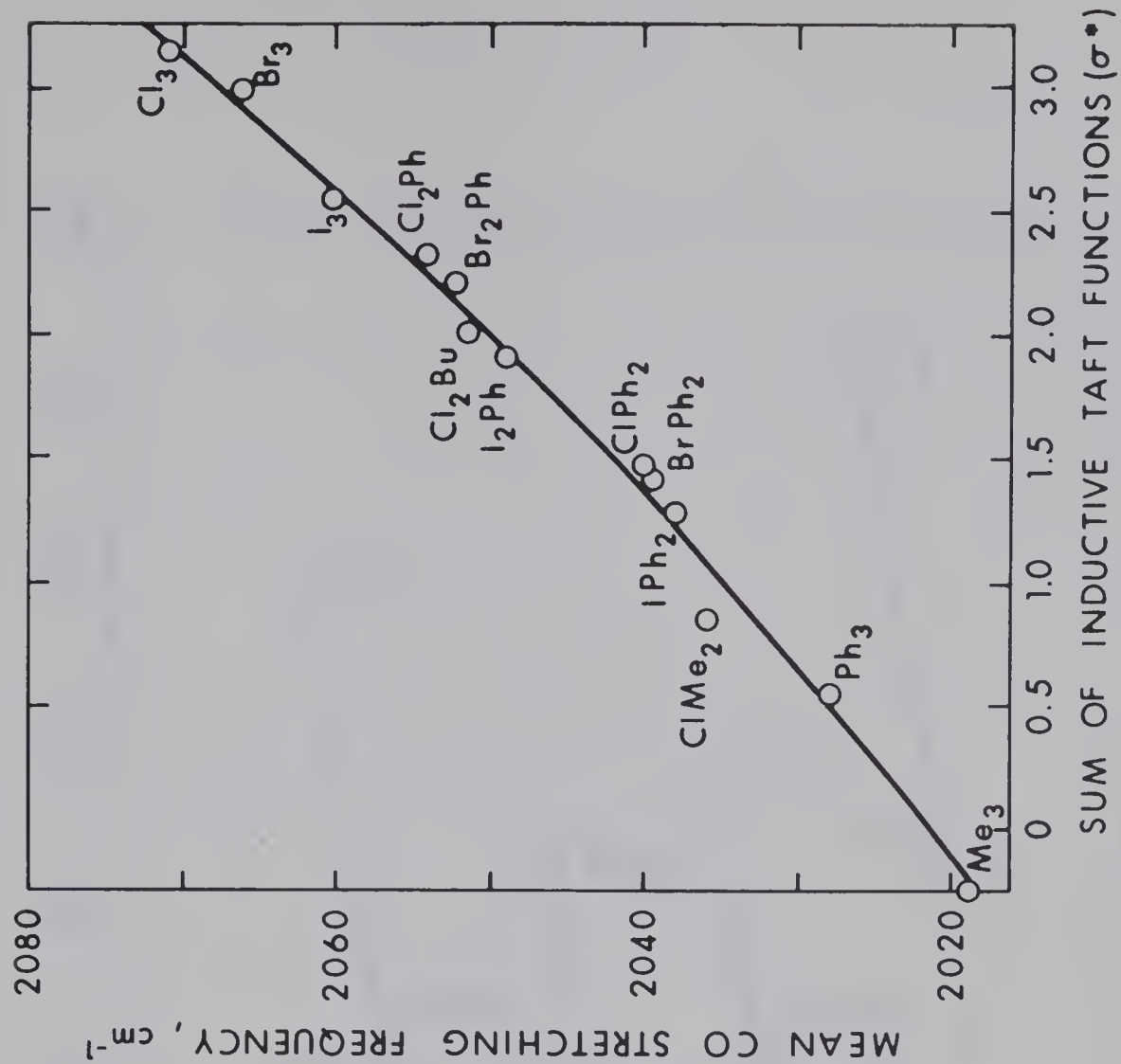


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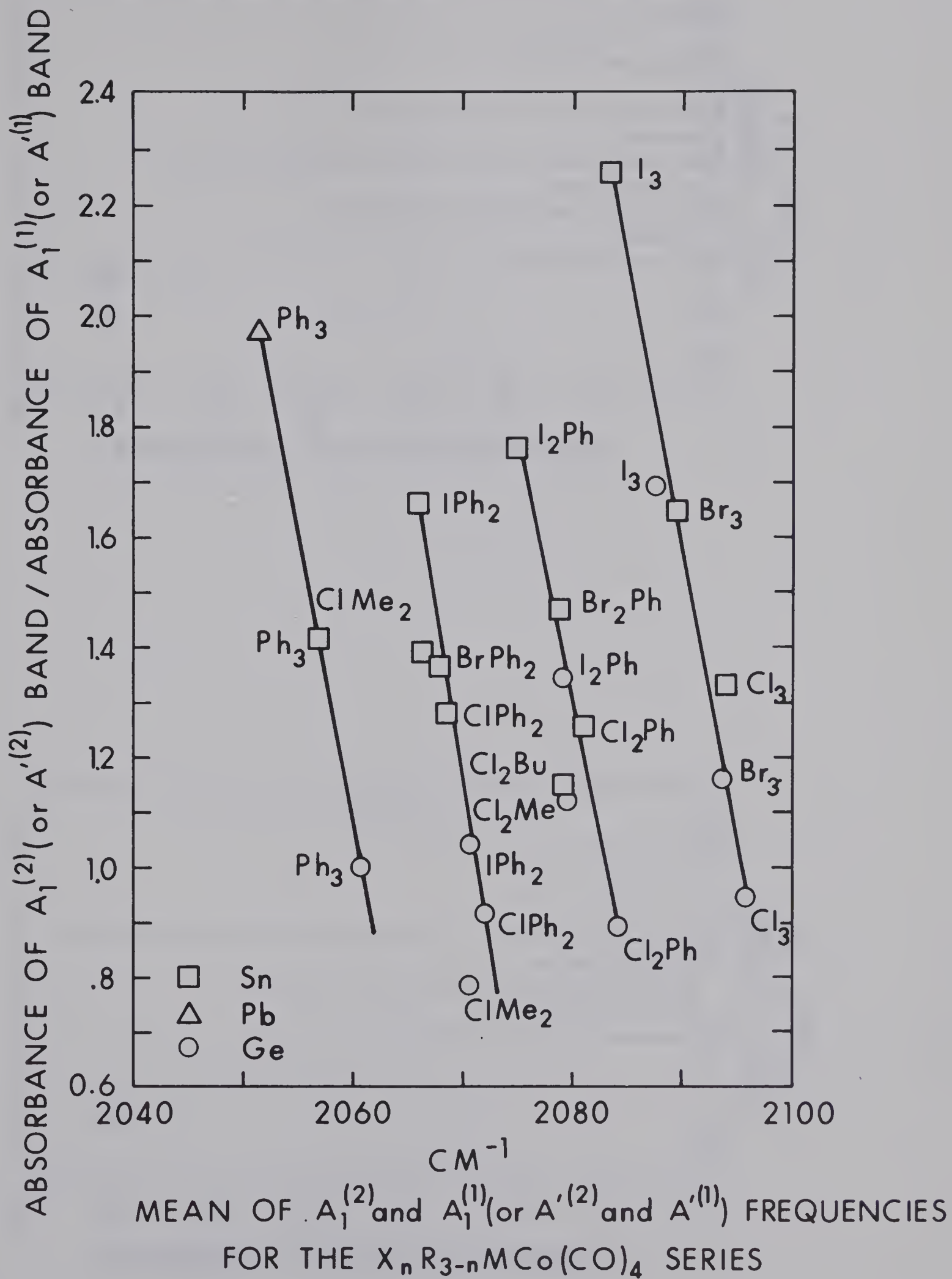


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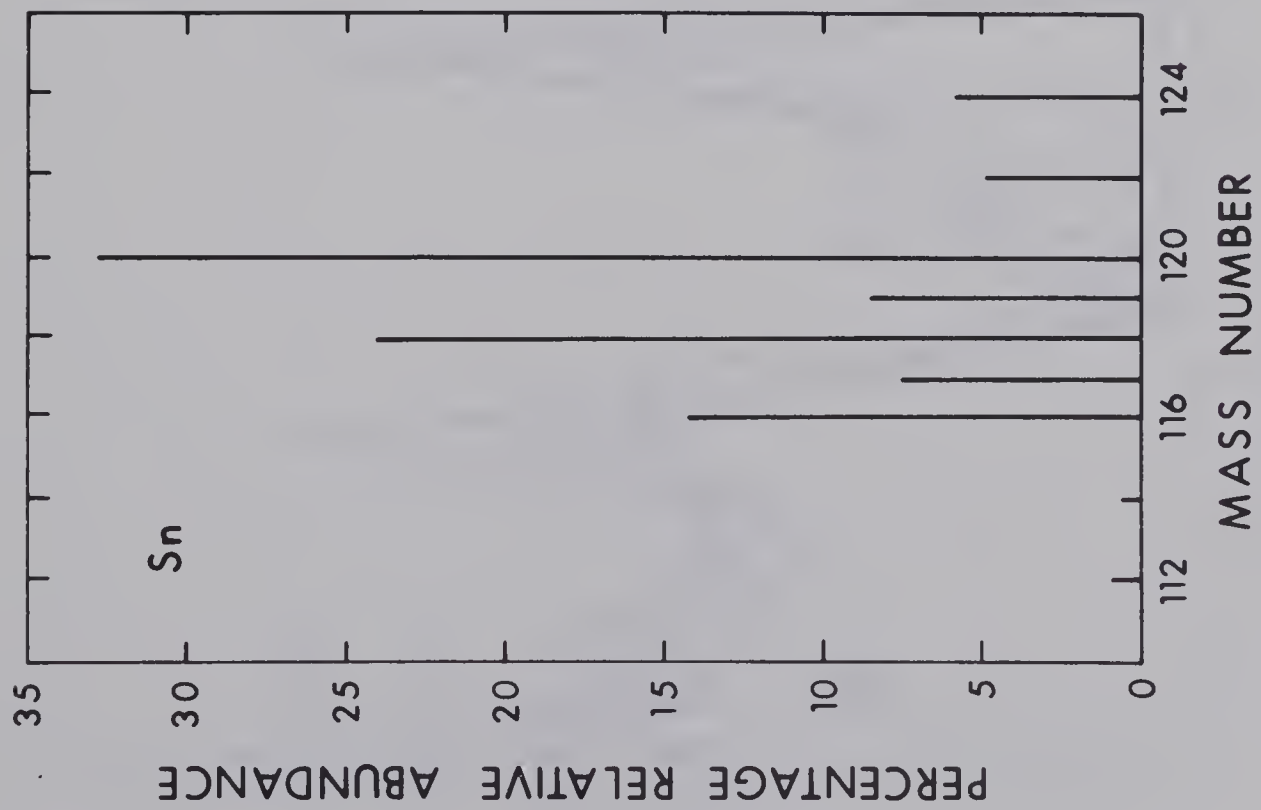


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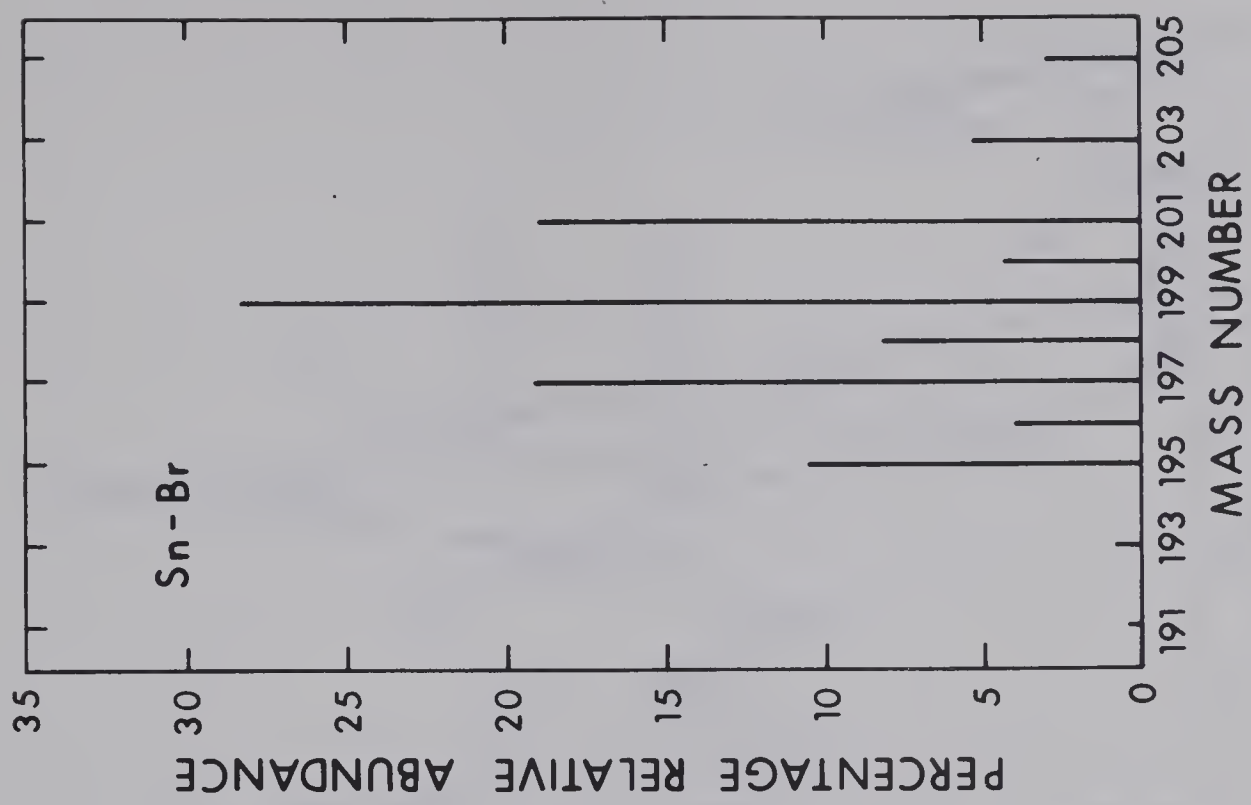


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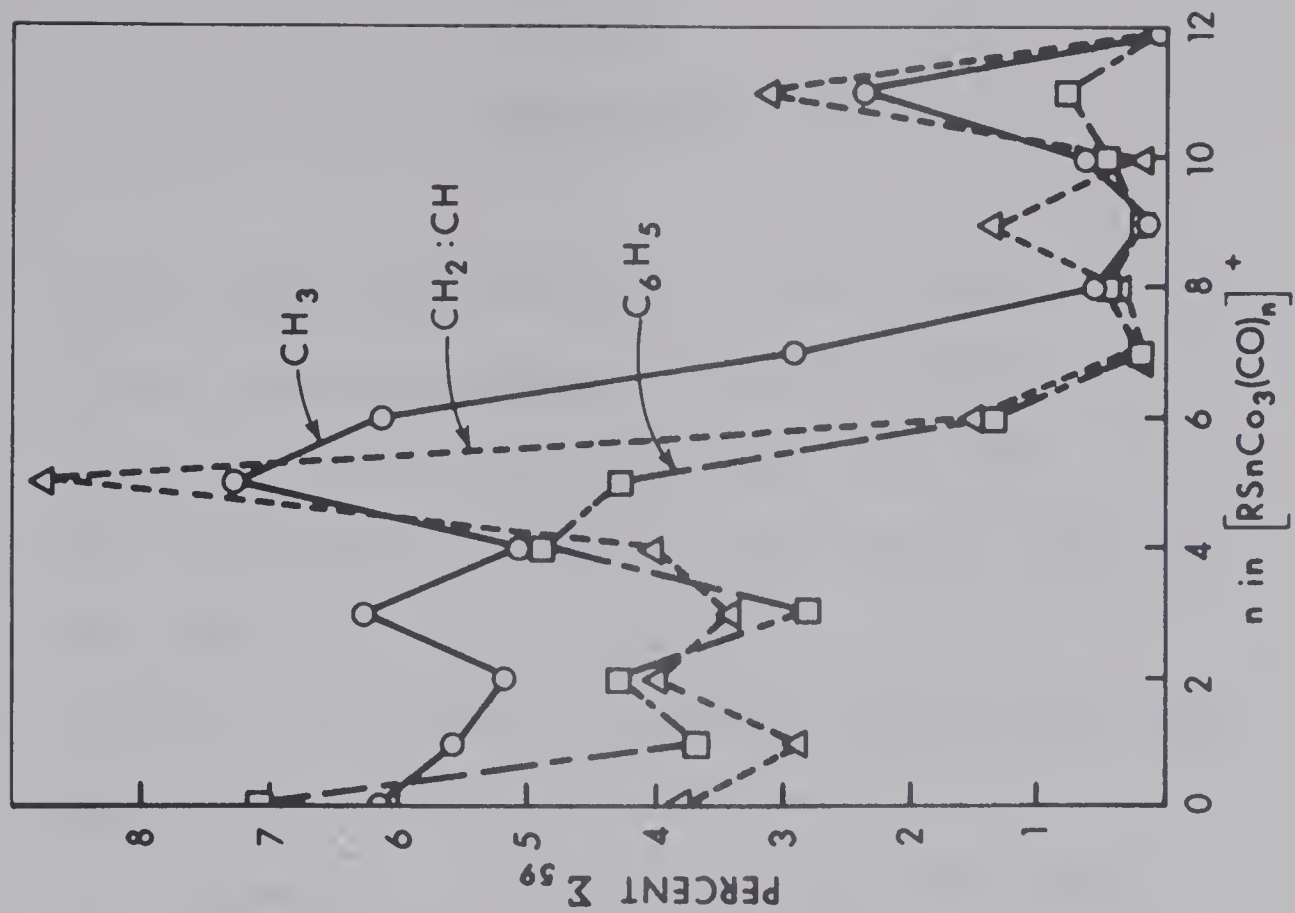


Figure 55

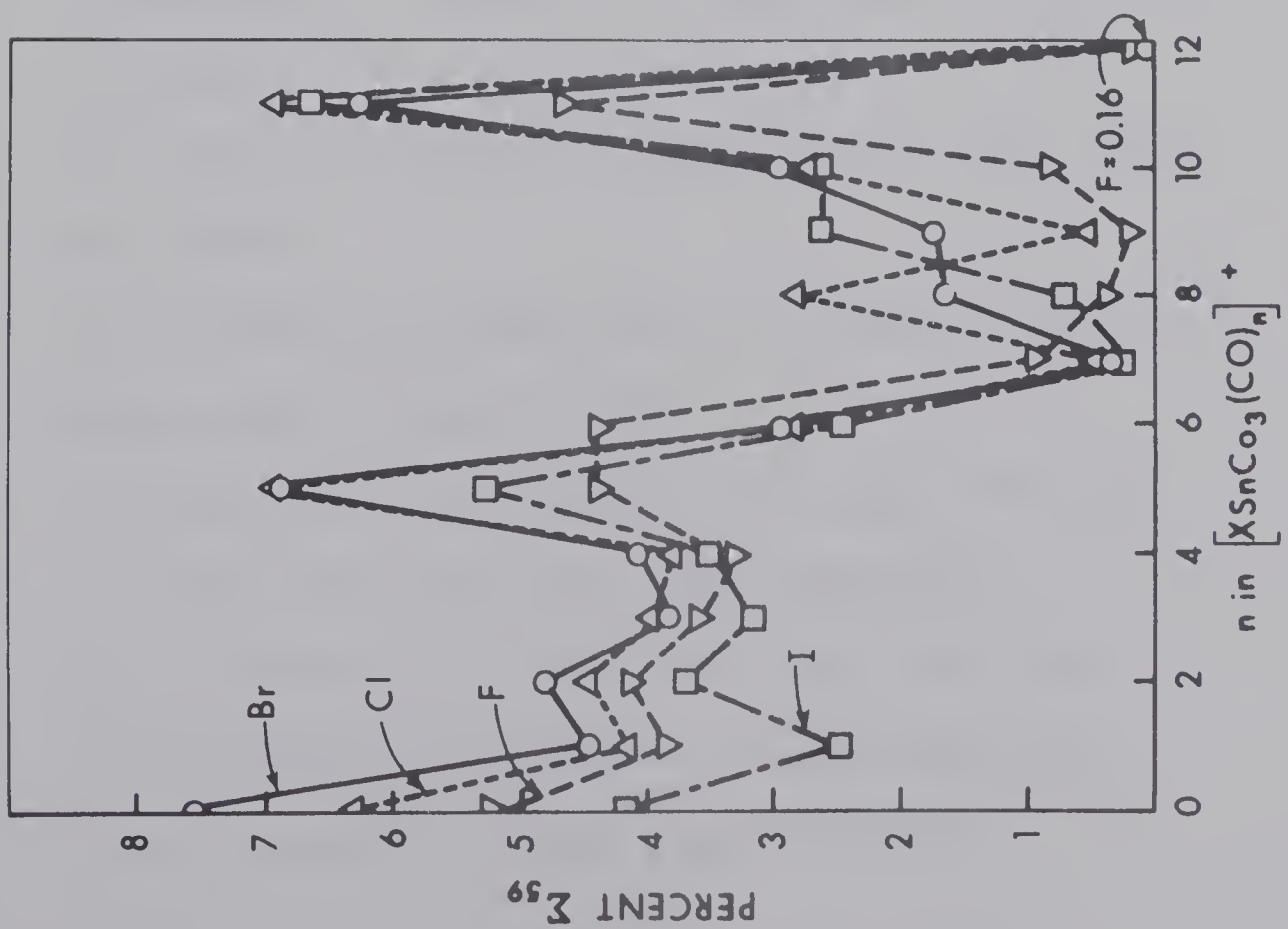


Figure 56

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CONCLUSIONS

1. In the present work the following previously unreported metal-metal bonds were formed: Ga-Co, Ge-Ni, Sn-Ni, Ga-Mn, In-Mn, In-Mo, and In-Fe.
2. Numerous examples of group III derivatives of cobalt carbonyl were synthesized for the first time and their properties investigated. Such compounds involved cobalt-gallium and cobalt-indium bonds.
3. An examination of synthetic methods was carried out. In particular, as a result of this work, the scope of the insertion reaction as a general method for synthesizing main-transition metal bonds, has been broadened and defined.
4. An extensive series of tin derivatives of cobalt carbonyl was synthesized, and their properties examined in some detail. These tin-cobalt derivatives now represent the most fully explored metal-metal bonded system.
5. The infrared spectra of the tetracarbonylcobalt derivatives were studied and assignments made for the mono(tetracarbonylcobalt) compounds. The variations in carbonyl stretching frequency were explained in terms of the influence of substituents on the π and σ character of the metal-metal bond. These initial results indicate that further more detailed studies of these compounds should throw more light on the nature of the metal-metal bond.

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